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THE

CHEMICAL GAZETTE,

OR,

JOURNAL OF PRACTICAL CHEMISTRY,

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS AND MANUFACTURES.

CONDUCTED BY

WILLIAM FRANCIS, PH.D., F.L.S., F.R.A.S., F.C.S.

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THE

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Colouring Matter of Fustic (Morus tinctoria).

By Dr. R. WAGNER.

THE wood of *Morus tinctoria*, Jacq. (*Broussonetia tinctoria*), known in commerce by the names of fustic and yellow wood, has been examined by Chevreul, George and Preisser, if any dependence can be placed in the statements of the latter. The first chemist devoted his attention more especially to the colouring matters contained in this wood, of which he found two possessing the property of dyeing stuffs, mordanted with alum, yellow. He called these substances *white* and *yellow morine*.

George furnished merely a superficial analysis of the wood. He states that it contains 15 per cent. of substances soluble in hot water, consisting of gum, tannic acid, colouring matter and gallic acid. Preisser's statements have been sufficiently refuted, both generally and specially, as regards different yellow and red pigments, by numerous chemists; and I have satisfied myself that his assertions regarding the colouring matters of the fustic* are totally without foundation.

At the very outset of my examination, I observed that I could only turn to account a few of the results obtained by Chevreul, as his experiments were not made with the pure pigments, as evident from his Memoir. Moreover, most of his statements refer to the behaviour of reagents, not to the colouring principles, but to a decoction of the wood.

My object was to prepare the colouring matters of the *Morus tinctoria* in a pure state, and to submit them to as complete an examination as possible. The following are the results I have obtained:—

Preparation of the Colouring Matters.—As directed by Chevreul, I exhausted the wood repeatedly with boiling water, filtered the decoction whilst boiling, and set the filtered solution aside for several days. A thick yellow sediment separated, which was collected on a filter and washed with cold water. This precipitate appeared

* Chem. Gaz., vol. ii. p. 431.

under the microscope to consist of bundles of sulphur-coloured crystals, and is the morine of Chevreul. A more accurate examination however showed me that this substance consisted of a large quantity of a peculiar tannic acid and a lime compound, which latter was only sparingly soluble in water, but easily soluble in alcohol. This lime compound contains the peculiar colouring principle of fustic, for which I retain the name of *morine* (moric acid).

Preparation of Morine.—To obtain this body in a pure state, I adopted, after numerous experiments, the following method:—

The wood is repeatedly exhausted by boiling with water; the decoctions are filtered boiling, and then evaporated until the quantity amounts to about 5 quarts for 5 kilogrms. of the wood. This concentrated liquid is then set aside. In the course of one or two days, a sediment of the above-mentioned compound, several inches high, has formed in the beakers, above which is a brown liquid, from which a little more of the yellow compound may be obtained by further evaporation and standing. This liquid contains principally the peculiar tannic acid occurring in fustic, which is also a pigment, and may be obtained by carefully evaporating the liquid in the water-bath to dryness. I shall call this acid *moritannic acid.*

The yellow compound collected on the filter is dissolved in alcohol after the greater portion of the liquid has been removed by pressure between blotting-paper, and the alcoholic solution poured into 8 to 10 times the quantity of water. By this means the compound of morine with lime is separated in yellowish-brown flakes, whilst the moritannic acid is held in solution. This operation is repeated three or four times. The separated morine-lime is collected upon a filter, washed with cold water, and dried.

This compound forms, when it has been dissolved and reprecipitated three or four times, a sulphur-coloured crystalline powder, which separates from its alcoholic solution in minute sulphur-coloured crystals. It burns upon platinum to a white ash, which consists solely of carbonate of lime. In two experiments I obtained 6·94 and 6·708 per cent. of lime. According to this, morine-lime contains on an average 6·8 per cent. of lime.

To obtain the pure morine from this compound, it is mixed with a quantity of crystallized oxalic acid corresponding to the amount of lime (about 12 per cent. of the weight of the morine-lime), and boiled with 15 to 20 times the quantity of alcohol of 0·876, the solution filtered hot, and the filtrate poured into 100 times the quantity of cold water. The morine separates immediately in the form of a yellowish-white crystalline powder, which may be obtained perfectly white by resolution in alcohol and precipitation with water. The precipitate is collected on a filter, and the morine thus obtained dried at 212°, excluding the air as much as possible. On combustion, it leaves no ash.

The morine separated from the morine-lime by acetic acid was of a yellowish-brown colour and not quite free from mineral constituents. Concentrated and dilute sulphuric acid too readily effect a decomposition of the morine to be used instead of oxalic acid.

Properties of Morine.—The morine separated from the lime compound in the above manner forms in the pure state a white crystalline powder, which very soon acquires a yellowish tint by exposure to the air. It dissolves scarcely at all in cold, and but sparingly in boiling water. 1 part morine requires 4000 parts of water at 68° F., and 1060 parts at 212° for its solution. The solution is nearly colourless, and deposits on cooling the greater portion of the morine. It dissolves readily in alcohol and æther. These solutions are of a dark yellow colour in a concentrated state. When mixed with water, the morine separates in bulky white flakes. Morine has a slightly bitter, but not astringent taste; the solutions have a slightly acid reaction. Chevreul states that the aqueous solution is precipitated by gelatine, which I could not confirm. Animal membrane, digested with an aqueous solution of morine, is coloured yellow; but the morine cannot be removed from the supernatant liquid either by solution of gelatine or by a fresh quantity of membrane.

An almost colourless solution of morine turns yellow in the air, but not from exposure to light. This colouring arises from an absorption of ammonia (formation of morine-ammonia), but not from an oxidation, as the yellow solution again becomes instantly colourless upon the addition of hydrochloric, oxalic or sulphuric acid. On exposing a colourless aqueous solution of morine with pure oxygen over mercury, I did not find the slightest colouring of the solution, and the volume of the oxygen was unaltered; ammonia, on the contrary, is rapidly absorbed by morine and its solution. An ammoniacal solution turns brown, and finally black, in the air. Acids then precipitate no morine, but a blackish-brown humus-like substance (metagallic acid?). I have not been able to obtain from morine any substance corresponding to the hæmateine of Erdmann.

Dupasquier used and recommended a decoction of logwood for detecting the presence of bicarbonate of lime in waters for drinking; the same has been done by Erdmann for a solution of hæmatoxyline, as the most delicate test for ammonia; a spirituous solution of morine may be used for the same purpose. Whilst distilled water, or well-water containing gypsum, when mixed with a drop of the above solution, does not change colour, water containing an alkaline carbonate instantly strikes a deep yellow colour; morine is so sensitive towards alkalies, that paper which has been imbued with an alcoholic solution of morine, and appears perfectly white, instantly turns yellow when a few puffs of tobacco are blown against it, or when it is suspended in an atmosphere containing ammonia. I found the behaviour of morine at a high temperature to differ totally from Chevreul's statements in his 'Chimie appliquée à la Teinture.' When heated in a bath of metal, it begins at 356° to part with water. At 482° it is still scarcely altered, and behaves towards reagents like morine which has not been heated. At 572° it turns black, disengages a large amount of carbonic acid, gives off a small quantity of a yellow oil, which condenses in the receiver into crystalline granules, which dissolve *easily* in water, and like morine are coloured garnet-red by

perchloride of iron. There is also formed a considerable quantity of spirole; but I shall subsequently return to these products of the decomposition of morine.

Morine dissolves in concentrated sulphuric acid with a yellow colour, and disengages the characteristic odour of castoreum or of *Jaune Indien*, which points to the presence of carbolic acid. From this solution the morine is precipitated apparently unaltered by water.

Concentrated nitric acid forms a reddish-brown solution, which, evaporated in the water-bath to remove the excess of nitric acid, gives off nitrous vapours, and deposits on cooling large yellowish-white prisms of a nitro-acid, which, when heated upon platinum foil, melt and then quickly burn away. Its potash salt detonates violently. With baryta and protosulphate of iron it forms a colourless solution; it is consequently the *oxypicric acid* of Erdmann, as nitrophenissic acid would have given a red solution (hæmatonitric acid). Will and Böttger have already pointed to the formation of oxypicric acid (styphnic acid) in the treatment of the extract of fustic with nitric acid.

Hydrochloric, oxalic, dilute sulphuric, phosphoric, tartaric and acetic acids dissolve morine to a colourless liquid, which, on supersaturation with a caustic or carbonate alkali, is coloured, according to its degree of concentration, yellow to dark brown. The dyers in many places turn this property of the acids to account, and moisten the shavings of the wood with vinegar, before preparing the decoction, in order to render the colour lighter.

Alkalies, both carbonate and caustic, dissolve morine with a beautiful yellow colour; the above-mentioned acids turn the solutions colourless.

Perchloride of iron strikes a garnet-red colour with an aqueous solution of morine, which had already been observed by Chevreul. The purity of morine can be ascertained by this reagent; the smallest quantity of moritannic acid is instantly detected by the blackish-green colour.

Protosulphate of iron gives an olive-green precipitate. Sulphate and acetate of copper are reduced on ebullition with morine and the addition of potash, with separation of protoxide of copper. Nitrate of silver is instantly reduced, especially on the addition of a few drops of ammonia. Protochloride of tin gives a lemon-coloured, alum with the addition of some ammonia a light yellow precipitate.

Analysis of Morine.—The substance employed for analysis was perfectly pure, whitish-yellow and crystalline; it experienced no loss in weight by drying at 248°, and furnished—

Carbon	55·19	55·14	56·06	18 =	108	55·102
Hydrogen ..	4·29	4·02	4·19	8	8	4·081
Oxygen	..	..	..	10	80	40·817

The reason why I adopt the formula $C^{18} H^8 O^{10}$, and not the simple expression $C^9 H^4 O^5$, will appear from the composition of moritannic acid.

To determine the atomic weight of morine, I employed the lead salt, which was prepared by precipitating an alcoholic solution of morine with an alcoholic solution of neutral acetate of lead. The yellow precipitate formed, on drying in the air-bath, a blackish-brown mass, which rubs to a brownish-yellow powder. Notwithstanding that I operated with a pure substance, the results of the analyses did not agree; the amount of lead varied between 44·1–45·6 and 47·2 per cent.; the equivalent of the acid, 124, 132, 140.

Morine gave no constant compounds with the alkalies. Boiled with recently-precipitated carbonate of baryta, I obtained from the morine, by evaporation of the baryta solution, a reddish-brown powder, morine-baryta, which furnished on analysis 22·8, 21·8 and 21·9 per cent. of baryta. The formula $C^{72}\,H^{32}\,O^{40}$, 3BaO would require 22·2 per cent. of baryta.

Admitting the saturating capacity of morine to be identical with that of moritannic acid, the rational formula of morine-baryta is—

$$3(C^{18}\,H^{7}\,O^{9},\,BaO)+(C^{18}\,H^{7}\,O^{9},\,HO);$$

or, as a tribasic substance,—

$$3(C^{18}\,H^{5}\,O^{7}\left\{\begin{matrix}BaO\\2HO\end{matrix}\right.)+(C^{18}\,H^{5}\,O^{7},3HO).$$

The morine-lime contained in the decoction of the wood has in the crystalline state the formula—

$$C^{18}\,H^{7}\,O^{9},\,CaO+C^{18}\,H^{7}\,O^{9},\,HO.$$

At 212° this compound loses 2 equivs. of water, and leaves—

$$2C^{18}\,H^{5}\,O^{7},\,HO+CaO,\,HO,$$

which formula requires 7·12 per cent. of lime.

[To be continued.]

On the Preparation of the Sesquisulphate of Iron. *By* A. Levol.

Nothing is more simple in appearance than the preparation of this sulphate. Having however required some very pure for delicate experiments, I was compelled to abandon the processes described, which all present more or less serious inconveniences when the object is to obtain a product the purity of which may be depended on. This led me to search for some other method of preparing the sesquisulphate in a chemically-pure state. The one I have adopted is most simple; and I should not have described it, had it not furnished me with the means of refuting an error into which almost all chemists have fallen. It is thought, that, in the action of hot concentrated sulphuric acid upon metallic iron, protosulphate of iron and sulphurous acid are formed at the same time according to the following equation:—

$$Fe+2SO^{3}\,HO=FeO,\,SO^{3}+SO^{2}+2HO.$$

Now the reaction is as follows:—

$$2Fe+6SO^{3},\,HO=Fe^{2}\,O^{3}+3SO^{3}+3SO^{2}+6HO;$$

that is to say, contrary to what is asserted, sulphate of the sesqui-

oxide of iron is formed. This method of preparing the sulphate is consequently most easy; in fact, after having added an excess of concentrated sulphuric acid to some fine iron wire, it suffices to heat until no more white vapours are perceptible. The operation may be made in a porcelain crucible.

If the reaction is as I have represented, it is evident the protosulphate may be substituted for the metallic iron; and, in truth, when this salt, having been *previously dried*, is treated with boiling concentrated sulphuric acid, there is a copious disengagement of sulphurous acid, and the residue, as in the first case, consists of sesquisulphate of iron. This reaction, I am informed, has already been turned to account in the arts, in order to procure the sesquisulphate. I should observe, that it is frequently requisite to repeat the action of the sulphuric acid on the product, in order that not a trace of protosulphate may remain. The sulphate thus obtained is exceedingly pure; it is of a dirty white colour, and dissolves with great difficulty in pure water; it requires several days to dissolve some grammes at the ordinary temperature; however, in the course of time water takes up a pretty considerable quantity. Its solution may be hastened by heat; but this must be very gentle, as it is known that the aqueous solution deposits a basic salt on boiling.

The sulphate of the sesquioxide of iron obtained with metallic iron and concentrated sulphuric acid is pure after the first treatment. It differs from the other by its colour, which is slightly pink. Do all the irons exhibit this peculiarity, or should it be attributed to traces of cobalt?—*Journ. de Pharm.*, Nov. 1850.

On a peculiar Metamorphosis of the Bile of the Ox.

By C. Enderlin, M.D.

Having in 1844 studied the influence of various organic acids and their salts, and acidulo-saccharine fruits, upon the properties and composition of the urine, in which I obtained the same results as those obtained by Wöhler and others, I was anxious to determine whether purified bile (then regarded as bilate of soda), when taken internally, was capable of altering the urine in the same manner as is the case with the alkaline salts of vegetable acids.

For this experiment, the bile removed from the gall-bladder of an ox, immediately after the animal was killed, was evaporated in a water-bath, and the residue treated with absolute alcohol to separate the mucus, the sulphate, &c. The alcoholic solution was decolorized with animal charcoal and preserved.

On the day of the experiment I evaporated the alcoholic solution, which had remained perfectly clear, on the water-bath, to the consistence of an extract, and dissolved it in pure water. The solution was slightly yellow, and had a barely-alkaline reaction. I could not take the whole of it; about the fourth part was left, and set aside in a beaker-glass covered with paper*.

* My urine remained acid, and neither by taste nor reagents could I detect any bile. The quantity of bile taken was evidently too small to convert the acid reaction into an alkaline one.

Some days afterwards the solution became opalescent, then turbid, finally milky, and a white flaky deposit appeared; but the liquid had still not become clear. It had however now acquired a very *strongly acid reaction.* The glass remained untouched for some days.

When I again examined it, I found the flaky precipitate changed into warty masses of a satiny lustre, covered with a number of fine silky prisms grouped in stellæ and aigrettes. The liquid was now perfectly clear, but still *just as acid.* Some days afterwards I found very long capillary prisms suspended in the liquid.

The whole was then thrown on a filter, the crystalline mass washed with water, which reduced its volume somewhat, and dried with the filter. To obtain more crystals, I evaporated the filtrate on the water-bath to one-third of its volume, during which yellowish-brown resinous drops separated, which were subsequently found covered on all sides with prisms, partly in stellæ and aigrettes, partly forming a network. The resinous drops *were hard.* As I regarded the resinous body as choloidic acid, I was in hopes of separating the crystals from it by water; but the resinous drops soon became soft, syrupy, and the water added became opalescent, subsequently milky; by the repeated addition of water, the whole became resolved into a milky liquid. In a short time a white flaky precipitate again subsided from the latter, and became converted into a voluminous network of fine prisms. The milky liquid ran through the filter, and again deposited prisms. Subsequently resinous drops appeared upon the sides of the vessel, and the liquid became clear *bilic acid.* The clear liquid was rendered milky by muriatic acid, slightly by acetic acid, and minute crystalline grains and *white oily drops* were deposited upon the sides of the test-tube, *bilic acid.* Basic acetate of lead produced a precipitate, for the greater part soluble in acetic acid. The brown resinous drops obtained on evaporation dissolved readily and completely after the separation of the adhering acid in pure water. The liquid was precipitated by mineral acids.

They therefore consisted of (unaltered?) *bilic acid.* The properties of the crystalline body however agreed in all respects with those given by L. Gmelin in regard to *cholic acid,* which he was the first to discover.

Strecker has shown that this is a normal and constant constituent of the bile, and has fully described its properties.

The substance I obtained fused upon platinum foil, at the same time frothing up considerably. A voluminous charcoal remained, which on incineration left a *considerable* spongy ash. The ash reddened turmeric very strongly, and effervesced with acids. The substance might therefore be regarded as acid choleate of soda. Dilute sulphuric acid threw down from its dilute ammoniacal solution a resinous precipitate, which during the night became converted into acicular groups, resembling wavellite. An alcoholic solution of it, when treated with a drop of acetic acid and left to spontaneous evaporation, deposited the substance in the form of a

syrupy mass, which after a further lapse of time also became converted into the above crystals. In another experiment, the crystals were feathery. When some of the grains of the crystals were carefully heated with a few drops of water and a trace of sulphuric acid upon platinum foil, or in a porcelain cup, they constantly assumed first a *deep sky-blue colour*, which was subsequently changed into a *blood-red*, occasionally *somewhat violet tint*. On the further application of heat, at first the most varied shades of yellow, brown, green, &c., such as are found in the bile of animals, were produced*. Now if, as will be seen from the following remarks to be very probable, the bile (and perhaps albuminous matters also) contains one or several bodies conjugate with sulphuric acid, the metamorphosis of a biliary matter into colouring matter of blood, just alluded to, would lose all its obscurity, and would render more intelligible the knowledge of the influence of the liver, or rather its secretion, upon the formation of the blood.

Further Description of the Acid Liquid poured off from the Substances separated.—The intensity of the acid reaction led me to suspect the presence of a mineral acid; and as I have repeatedly found in the cinder and ash of glandular organs, especially the spleen, the liver and the pancreas of different animals, acid phosphates and metaphosphates, and as Braconnot, and subsequently Fremy, state that they have found in the liver a fat containing phosphorus (phosphoric acid), I at first suspected *free phosphoric acid*. This supposition was not however confirmed, but I found *a large quantity of free sulphuric acid* present. The following are the experiments:—

a. On evaporating a small quantity of the liquid upon platinum, vapours were evolved, which strongly reddened litmus and gave a distinct odour of sulphurous acid. After incineration, a neutral ash remained, in the aqueous solution of which a barytic salt detected a considerable quantity of sulphuric acid.

b. On neutralizing the liquid with barytic water, a copious precipitate of $BaO\,SO^3$ was immediately produced. The filtrate, when evaporated and incinerated, left a residue of carbonate of baryta.

c. On neutralizing a larger quantity with carbonate of soda, evaporation to dryness, exhaustion of the residue with absolute alcohol, subsequent solution of the residue in water and evaporation, I obtained crystals exhibiting the form and characters of sulphate of soda. I sought for taurine in the liquid, but could find none. These experiments appear to me to leave no doubt of the presence of free sulphuric acid. But whence its origin? At the time the observation was made, all the conditions requisite for solving this question were absent. It could not possibly have arisen from the sulphates mixed with the unpurified bile, and which may be separated without the decomposition of the organic matter, as traces

* I first observed this beautiful reaction in 1842; and am also satisfied that bilic acid affords the material for the formation of the *red* colouring matter of the blood (as also of the *blue* detected in the blood of the ox by Sanson), under the influence of sulphuric acid either already formed or in a nascent state.

only of these are taken up by absolute alcohol; moreover, the quantity of sulphuric acid in the form of sulphates is small, and the separation of the acid from them in a free state would be without analogy. The free sulphuric acid, or its elements, must have existed in organic combination with the elements of some constituent of the bile! M. Enderlin is inclined to believe that the explanation of this remarkable occurrence is to be found in the circumstance, that the bile contains one or more conjugate compounds of SO^3 or SO^2 in an indifferent or neutral form (in combination with soda), which under certain circumstances might possibly become converted into SO^3 and other bodies, which future investigations must determine; perhaps sulphate of glycerine ?, which M. Pelouze supposes to occur in the yolk of the egg.—*Ann. der Chem. und Pharm.*, vol. lxxvi. p. 154.

On the Sulphuret of Nitrogen. *By* J. M. Fordos *and* A. Gelis.

M. Soubeiran has assigned to the sulphuret of nitrogen the formula S^3N, based principally upon the action which boiling water exerts upon the compound. In this reaction, 3 equivs. water are supposed to be fixed, nothing eliminated, whence results a salt having the formula S^3O^3, NH^3, Aq, that is to say, a sesquihyposulphite of ammonia.

This assertion leads us to doubt the accuracy of the observation, for at present only neutral hyposulphites, having the formula S^2O^2, MO, are known. It appeared first of all desirable that the action of water upon the sulphuret of nitrogen should be examined afresh, and we were engaged in this investigation when M. Laurent published his views concerning the constitution of the ammoniacal compounds in the 'Revue Scientifique.' In that memoir he admits that the formula of the compound known by the name of sulphuret of nitrogen should be changed, asserts that this substance must contain hydrogen, and be represented by S^2HN, and that consequently it is not a sulphuret of nitrogen.

The results which we had obtained, although opposed to those of M. Soubeiran, did not allow of our adopting the new formula; but as the assertions of M. Laurent were supported by some experiments, we thought it right to begin ours afresh. Being at present certain of the accuracy of our first results, we lay them before the public.

When ammoniacal gas acts upon perchloride of sulphur, these two substances experience a series of metamorphoses, and there is finally obtained a yellow powder, which M. Soubeiran erroneously considered to be a simple substance, and to which he applied the name of biammoniacal chloride of sulphur.

This powder, from which we have been able to extract, by means of solvents, no less than five substances, furnishes, on treatment with sulphuret of carbon, at the same time sulphur and a beautiful orange-yellow product. By washing repeatedly, and in the cold, with small quantities of sulphuret of carbon, the whole of the sul-

phur is removed. On then treating the mass with the same solvent, and boiling until it no longer colours it, the orange-coloured substance is dissolved, and again deposited on evaporation in the form of crystals. This is evidently the substance which was examined, in a more or less impure state, by M. Soubeiran, under the name of sulphuret of nitrogen, as it possesses most of the properties pointed out by that chemist.

The sulphuret of nitrogen in the pure state forms transparent rhomboidal prisms, the powder of which is of a most brilliant yellow colour; but this powder must not be prepared without precaution, for a slight shock upon a hard body suffices to produce a lively detonation. 5 centigrms. of sulphuret of nitrogen, placed in an agate mortar and struck with the pestle, gave a report similar to that of a musket, and the pestle and mortar were broken into several pieces. When touched with an ignited body, it melts without detonating. When heated in an oil-bath in a tube closed at one end, it is destroyed, with explosion, at about 315° F., liberating nitrogen, sulphur and traces of the undecomposed substance. In the state of powder, it has a faint odour, and acquires by friction the property of adhering to glass and paper in a high degree. Its action upon the mucous membranes is very irritating; water scarcely moistens it, and does not dissolve it; alcohol, æther, wood-spirit and essence of turpentine dissolve small quantities of it; but the best solvent is the sulphuret of carbon. This is not absolutely without action upon it, but it is slow, and requires much time before it is complete; it is however a very remarkable one; we have seen solutions of sulphuret of nitrogen in sulphuret of carbon become completely colourless in a few months, and we found in the products hydrosulphocyanic acid, and a golden yellow deposit, which had the appearance of the substance known by the name of sulphocyanogen or of cyanoxysulphide.

The analysis which we made of this substance leads to none of the formulæ assigned to that body; but as we possess no very positive data respecting the composition of sulphocyanogen, we intend to study the two bodies comparatively as soon as we have obtained a sufficient quantity.

Analysis of the Sulphuret of Nitrogen.—We carefully sought for the presence of hydrogen, and in all the experiments employed a considerable quantity of substance, in order to diminish as much as possible the chances of error:—

0·5 grm. of sulphuret of nitrogen furnished					0·015	water.	
0·5	...	...	...	...	0·045	...	
1·0	...	...	...	...	0·004	...	

These results, especially the last, sufficiently prove that the substance examined contains no hydrogen, and that consequently the formula proposed by M. Laurent must be rejected. That formula appears to belong to another substance.

Having proved that the compound under examination contains no hydrogen, and that consequently it is a sulphuret of nitrogen, it will

be easy to show that it has not the composition assigned to it by M. Soubeiran; that chemist's formula requires 77·32 per cent. of sulphur and 22·68 of nitrogen. The numbers we obtained are widely different, and correspond to the formula S^2N, viz.

Sulphur	69·47	68·83	69·95	69·06	2	= 69·56
Nitrogen ..	30·38	31·01	30·50	..	1	30·44

These results are likewise confirmed by the examination we have made of the action of water and the alkalies upon this body. According to M. Soubeiran, cold water acts slowly upon the sulphuret of nitrogen, converting it into hyposulphite of ammonia; the decomposition is very rapid when heat is employed, and the salt contains 1 equiv. of ammonia for $1\frac{1}{2}$ equiv. of hyposulphurous acid. According to the same chemist, alkaline solutions convert the sulphuret of nitrogen into ammonia and hyposulphurous acid. These different assertions are not admissible; in fact, the decomposition by water, as indicated by M. Soubeiran, would be represented by the formula $S^3N+4HO=S^3O^3, NH^3, HO$. Now in this reaction, supposing the formula of the sulphuret of nitrogen, S^3N, to be accurate, which is not the case, no gas would be disengaged, whilst it is very easy to prove that in this reaction ammonia is liberated. It is also found that the liquid possesses all the characters of a mixture of hyposulphurous acid and of an acid of the thionic series.

The analyses of the products showed that the reaction of water upon the sulphuret of nitrogen should be represented by the following equation:—

$$4(S^2N)+9(HO)+Aq=S^2O^2, NH^3, Aq+2(S^3O^5, H^3N, Aq)+H^3N.$$

This formula explains all the phænomena observed, and its accuracy is placed beyond doubt by the reaction of potash upon the sulphuret of nitrogen, which may be represented as follows:—

$$2(S^2N)+3(KO)+6(HO)=S^2O^2, KO+2(SO^2, KO)+2(NH^3).$$

A hyposulphite and a sulphite are formed in such proportions that each of the two salts contains an equal amount of sulphur. These products are evidently due to two reactions, that of water upon the sulphuret of nitrogen, and that of potash on the trithionic acid produced in the first reaction. It is well known that this acid is resolved by alkalies into sulphite and hyposulphite—

$$2(S^3O^5)+5KO=S^2O^2KO+4(SO^2KO).$$

Comptes Rendus, Nov. 18, 1850.

✓ *On some Red Compounds of Uranium.* *By* A. Patera.

In the course of this year I was requested to find out some method of testing, as quickly and accurately as possible, the uranium ores of Joachimsthal, as to the amount of uranium they contained. In solving this question, the results of which I have already communicated*, I was led to examine several of the compounds of ura-

* Chem. Gaz., vol. vii. p. 228.

nium, and I found that the compounds of this rare metal still offer a wide field for investigation. Much has been done by the interesting researches of Arvedson, Peligot, Ebelmen, Wertheim, Rammelsberg, and many others; but yet entire chapters, as the sulphur compounds, are nearly quite unknown. I examined some new compounds discovered in the course of my investigation, and will here communicate the results of this examination, to be followed by several others, if the circumstances allow of my attending further to the subject. When a purified solution of a salt of the oxide of uranium, nitrate or muriate, is precipitated according to the method described by Wöhler with hydrosulphate of ammonia, a bulky brown precipitate is obtained, the colour of which on standing gradually passes into a reddish-brown, and finally, after from twenty-four to twenty-eight hours, into a dark blood-red. The change of the brown into the red colour takes place very gradually, and the precipitate is not observed to become red from the surface, as in the case of the oxidation of the protoxide of manganese, where the dark colour of the oxide is first evident on the surface, whence it extends further. The precipitate retains its beautiful red colour when collected on a filter, washed with hot water, and dried at 212°; it only becomes somewhat darker and less brilliant.

Berzelius and Gmelin state in their manuals, that the precipitate of the sulphuret of uranium is at first black, and turns to an orange colour on the surface by being exposed to the air for a week or so. Berzelius states that this is probably an oxysulphuret, and observes that the same compound is obtained when sulphuretted hydrogen is passed through oxide of uranium recently precipitated by ammonia.

I examined the dry precipitate. It is easily soluble in muriatic acid, sulphuretted hydrogen being evolved and sulphur eliminated. The solution contains oxide of uranium. When heated in a flask, water escapes, sulphur sublimes, and the odour of ammonia becomes perceptible; a green powder is left, which, on being treated with muriatic acid, disengages sulphuretted hydrogen. When heated in the air, the sulphur is completely burnt, and a dark green protoperoxide remains, the weight of which corresponds to 71 per cent. of pure uranium. The amount of sulphur which was precipitated as sulphate of baryta by chloride of barium from a solution of the salt in nitromuriatic acid, amounted to 2·75 per cent. of the salt employed. The relative quantities of the constituents of this compound could not be made out more accurately, as the separation of uranium from ammonia, and the quantitative determination of the latter body, offer considerable difficulty. I attempted therefore to replace the ammonium in the compound by a body which could be more easily estimated, and selected potassium for the purpose. The red ammonium salt, on being boiled with a solution of caustic potash, gave off ammonia; the bulky precipitate shrunk to a more pulverulent one, but still retained its beautiful colour. As soon as the smell of ammonia ceased, the precipitate was washed with hot water, dried at 212°, and submitted to further examination; the red salt, when heated with access of air, turned pale orange-yellow, and

lost 8 per cent. in weight. The quantitative analysis, made in the usual manner, gave in 100 parts—

Uranium	65·57
Potassium	10·60
Sulphur	1·44
Water	7·50
	85·11

14·89 wanting, was brought into calculation as oxygen.

Now if we divide the numbers found by the corresponding atomic weights, taking that given by Ebelmen for uranium =742·87, we obtain—

88 atoms of uranium.
22 atoms of potassium.
7 atoms of sulphur.
67 atoms of water.
148 atoms of oxygen.

Now if we take 63 atoms of water instead of 67, and 147 atoms of oxygen instead of 148, which may the more readily be done, as this amounts in the composition in the first case to 0·6 per cent., and in the latter case to 0·1 per cent. difference, these two constituents being moreover calculated from the loss, we obtain the formula—

$$2U^2, S^3, KS + 21(2U^2O^3, KO + 3HO),$$

which, calculated for 100 parts, gives—

Uranium	65·9
Potassium	10·8
Sulphur	1·4
Oxygen	14·8
Water	7·1,

which agrees pretty well with the results of the analysis.

At first sight the formula appeared to me so unusual, that I suspected the substance examined to be a mixture, and not a true chemical compound; on further consideration, however, my doubts vanished. When a solution of the oxide of uranium is precipitated by caustic potash, and the washed precipitate dried, a compound having a very similar constitution is obtained, viz. biuranate of potash with 3 atoms of water; on ignition the water is expelled, and there is left anhydrous biuranate of potash. This same compound also remains when the red potash salt is deprived of its 3 atoms of water by ignition. The resemblance of the two salts would be still more remarkable if we were also to conceive the sulphuret combined with 3 atoms of water, and wrote the formula as follows:—

$$(2U^2, S^3 + KS + 3HO) + 21(2U^2O^3, KO + 3HO).$$

This formula would accord better with the amount of water found than the first, as it requires for its formation 66 atoms of water, whilst the analysis gave 67; but I was still more afraid of going against probability, as the sulphosalts generally contain no water.

According to this view, the red salt is a biuranate of potash, in which a portion of the oxygen is replaced by sulphur. A further proof that it is not a mere mixture is, that other bases may be substituted for the ammonia, and similarly constituted salts of potassium, sodium, barium and strontium obtained when the ammonia salt is boiled with the oxides or chlorides, or when a solution of oxide of uranium is precipitated by the sulphurets of these metals. I prepared in the latter manner the potassium, sodium and barium salts; the last, however, contained a considerable amount of carbonate of baryta.

The red baryta and strontia salts, prepared by boiling the ammonium salt with chloride of barium or chloride of strontium, are converted on calcination into dark yellow acid salts of uranium; and they then, if they are pure, dissolve entirely in muriatic acid; but if they still contain any of the ammonium salt, which is the case when they have not been boiled sufficiently long, a dark green residue remains of protoperoxide of uranium, which is insoluble in muriatic acid.

The barium salt furnished on analysis—

Uranium	60·85
Sulphur	1·31
Barium	17·54
Water	6·59
	86·19
Oxygen	13·81
	100·00

The red salts of potassium, sodium, ammonium, barium and strontium may be boiled for a long time without losing their beautiful colour; but on attempting to substitute calcium or magnesium for the ammonium, a red salt is first obtained, which on boiling quickly turns black. The black salt dissolves in muriatic acid; it however no longer contains oxide of uranium, but protoxide.

I made some experiments with a view to the application of the red potash salt as a colour for painting. It furnishes, when ground with poppy oil, the most magnificent red; but the tendency to oxidize is so strong, that it soon acquires a yellowish tint, and loses much of its brilliancy. There is also another evil; as sulphuret it blackens the lead colours, which are so much used in oil-painting, sulphuret of lead being formed. Most of the varnishes likewise contain oxide of lead, and consequently destroy the red colour. The first evil however might perhaps be avoided by employing the barium salt, whilst the turning black might be obviated by employing oxide of zinc or artificially prepared sulphate of baryta instead of carbonate of lead. Mixed with gum or sugar, the potash salt retains its lively colour much longer; in the course of time however it also becomes yellowish.—*Journ. für Prakt. Chem.*, Nov. 1850.

On some Yellow Colours for Calico-Printing.
By C. H. Barreswil.

The two following receipts are extremely simple, but I do not find that they have ever been published. The first was suggested by the memoir of M. Braconnot upon the application of the yellow of arsenic. Instead of orpiment, I propose the chromate of zinc. I turn to account its solubility in ammonia, and the property which the ammoniacal compound possesses of being decomposed by a gentle heat, with reproduction of the chromate of zinc, like the solution of the sulphuret of arsenic.

The second recipe was suggested by the recent experiments of M. Broquette on the animalization of cotton tissues. The process consists in adding *picric* acid to a viscous solution of egg-albumen, which mixes with the matter without coagulating it, and remains intimately united after coagulation.

The proportion of the picric acid varies with the intensity of the yellow required.—*Journ. de Pharm.*, Nov. 1850.

ANALYTICAL CHEMISTRY.

On a new Method of decomposing Silicates in the Process of Analysis. *By* Henry Wurtz *of New York.*

Having had occasion, in the course of some researches upon the greensand of New Jersey, to observe the facility with which that substance is decomposed by fusion with chloride of calcium, it occurred to me that this property of the earthy chlorides might be applicable in the analysis of minerals.

Some experiments were accordingly made with reference to this supposition. Felspar and hornblende were fused with chloride of calcium, and it was found that the masses thus formed could be entirely decomposed by hydrochloric acid. The use of chloride of calcium is however obviously attended with several inconveniences, such as its deliquescent properties, the unavoidable introduction of a large quantity of ammoniacal salts into the solution, and in the separation of the lime from it.

Chloride of barium was therefore substituted, and the results of experiments upon this reagent were completely successful.

The chloride of barium of commerce often contains lead, resulting probably from the leaden vessels in which it is crystallized. It is necessary in this case to pass sulphuretted hydrogen through its solution. This solution is then filtered, recrystallized, and the washed crystals dried on the sand-bath, and ignited to drive off the water of crystallization. The pure chloride of barium thus obtained is pulverized, and is then ready to be used for the purpose here proposed.

Chloride of barium may be fused in a platinum crucible by a blast lamp, or by an alcohol blowpipe lamp. A mixture of chloride of barium and chloride of strontium in atomic proportions fuses however far more easily than either of its ingredients. Such a mixture is fused by the heat of an ordinary Berzelius lamp, and more easily, I think, than carbonate of soda. This is analogous to the well-known fact, that a mixture of carbonate of soda with carbonate of potash fuses more easily than either of the alkaline carbonates by itself. I have found, moreover, that although sulphate of strontia, when precipitated by itself, appears in a form somewhat gelatinous, tedious to wash and difficult to filter, yet when precipitated in the presence of sulphate of baryta, it assumes the finely-granular form of the latter, and the combined sulphates are as easily washed as the sulphate of baryta when precipitated alone.

The atomic proportions of a mixture of chloride of barium and chloride of strontium, suitable for the fusion of silicates, are about 4 parts of the former to 3 of the latter.

The best mode of proceeding was found to be as follows:—

The mineral in fine powder is intimately mixed with 4 or 5 times its weight of chloride of barium, or of the mixture of chloride of barium and chloride of strontium, in a platinum crucible, which is then covered, and exposed to a heat sufficient to fuse the mass for twenty or thirty minutes. When cool, the mass is loosened by bending the crucible, and allowed to fall into a beaker glass. Water is then poured on it in sufficient quantity to dissolve the excess of chloride of barium or chloride of strontium, and the undissolved portion allowed to subside to the bottom of the beaker. The clear solution is then poured off into a porcelain dish, and concentrated hydrochloric acid is poured upon the residue in the beaker. The precaution of removing most of the earthy chlorides by means of water before adding the acid, is necessary on account of the difficulty of decomposing the mass by the direct affusion of strong hydrochloric acid, owing to the insolubility of the chlorides of barium and strontium in this acid.

After the application of heat to the beaker until the residue contained in it is decomposed by the acid, its contents are also transferred to the porcelain dish, and the whole contents of the latter evaporated to dryness in the usual manner, for the separation of the silica. The filtrate from the silica is precipitated while hot with a slight excess of sulphuric acid, kept hot for half an hour, and then filtered. The filtrate from the sulphate of baryta must contain all the constituents of the mineral except the silica, and these may be determined by the ordinary methods.

When the mineral thus treated contains sulphuric acid, it will evidently remain with the silica in the form of sulphate of baryta. A difficulty would also seem to occur when the mineral contains much lime, on account of the insolubility of its sulphate. This last difficulty is however obviated, in some degree, by the very considerable solubility of sulphate of lime in hydrochloric acid, a fact which must have been noticed by many chemists.

The first qualitative experiment was made with a specimen of colourless, transparent orthoclase from New York Island. This felspar was fused with chloride of barium, according to the above process; and the silica thus obtained was found, upon fusion with carbonate of soda, to be perfectly pure.

The next experiment was made upon a black crystallized hornblende, from Franconia, New Hampshire. The silica obtained from this was found to contain considerably more than a trace of iron. I do not therefore venture to recommend this process at present for minerals which contain a very large quantity of oxide of iron. Many more experiments, which time has not permitted me to perform, will soon be made to settle this question, which I do not consider yet determined.

To test the chloride of barium process quantitatively, the mineral called pink scapolite, of Bolton, Massachusetts, long ago analysed by Dr. Jackson, was selected. My results agree entirely with his, except as regards the presence of lithia and oxide of cerium, which careful qualitative examination did not enable me to detect.

This mineral was found, contrary to recorded statements, to be not completely decomposed by concentrated acids, even when finely elutriated. A determination of the silica, made by decomposition with hydrochloric acid, gave the per-centage 50·25; another, made by fusion with carbonate of soda, gave 47·55.

Two determinations of the specific gravity, made upon the identical portion of mineral which was analysed, dried at 212° in coarse powder, gave the numbers 2·7002 and 2·7046.

The results of a fusion with chloride of barium were as follows:—

		Oxygen.	
Silica	47·67	24·78	24·78
Alumina	25·75	12·035	12·71
Peroxide of iron	2·26	0·68	
Lime	17·31	4·82	7·08
Soda	7·76	2·26	
Protoxide of manganese	trace		
	100·77		

agreeing nearly with the received formula of scapolite—

$$3(CaO, NaO)\,2SiO^3 + 2AlO^3, SiO^3,$$

which requires for the oxygen of the protoxides, peroxides and silica the ratio 1 : 2 : 4, while the above analysis gives the ratio 1·14 : 2·06 : 4.

This method appears to possess advantages for decomposing silicates which contain both the alkalies, over the ordinary methods of fusion with the hydrate or with the carbonate of baryta. Hydrate of baryta generally acts upon the crucible, causing the mass to adhere to it; and upon the affusion of hydrochloric acid, any potash which the mineral may contain consequently enters into combination as bichloride of platinum and potassium, and remains with the

silica. The carbonate of baryta process requires an intense heat, and is difficnlt of execution.

The chloride of barium process proposed in this paper is probably not more laborious than an ordinary carbonate of soda fusion, and is applicable in cases in which the silicate contains both potash and soda.—Silliman's *Journal*, November 1850.

On the Estimation of Sulphur in Volatile Organic Compounds. By Dr. H. Debus.

In my investigations of the products of decomposition of the binoxysulphocarbonate of æthyle, I have repeatedly observed that the usual methods of estimating the sulphur in volatile bodies not only present great difficulties in the execution, but likewise furnish very unsatisfactory results. After many endeavours to avoid these evils, I have adopted a process which can not only be readily employed for all solid and liquid substances, but leaves nothing to be desired as regards the accuracy of the results.

When a substance, on treatment with any reagent, parts with its sulphur in a determinable form, as for instance thialdine with nitrate of silver, there is no difficulty in ascertaining the quantity of this element. Substances which do not possess this property, and whose boiling-point is situated below the temperature at which chlorate of potash or nitre is decomposed, are usually analysed by passing their vapour over an incandescent mixture of some oxidizing compound with carbonate of potash or soda. If the substances are burnt with a mixture of chlorate of potash, or nitre and carbonate of potash, the combustion-tube is filled with an atmosphere of oxygen, which mixes with the vapour of the substance to be burnt, and destroys the latter by oxidizing its elements. Now it not rarely happens that the combustible gaseous compounds mix with the oxygen in such proportion as to cause explosions. Although with substances which are not very volatile this evil can be pretty easily avoided by increasing the relative amount of oxygen and burning very slowly, this is extremely difficult with highly volatile compounds; for towards the end of the combustion, when the amount of the oxygen liberated decreases considerably, it is frequently observed, that either the substance passes off unconsumed, or explosions occur.

Fresenius, in his Introduction to Quantitative Chemical Analysis, recommends a mixture of nitre and carbonate of baryta as combustion-agent: besides the above difficulties, this process has another source of error, which can scarcely be avoided. On the melting of the nitre, potash is set free, which at the high temperature attacks the glass, and forms with the constituents of the latter and the baryta, silicates insoluble in muriatic acid, which contaminate the sulphate of baryta formed. Zeise was accustomed to burn the compounds, whose amount of sulphur was to be determined, with a mixture of oxide of copper and carbonate of potash. After the combustion, some oxygen was passed for some time over the mixture in the combustion-tube, in order to oxidize any metallic sulphuret

which might have formed. In many cases, where I employed this method, I obtained too little sulphur; but, on the other hand, a black *sulphurous* residue, which, on digesting the ignited contents of the combustion-tube with muriatic acid, was left behind insoluble. This was probably a mixture of an oxide with an oxysulphuret of copper. There is also another difficulty to contend with in this process. It is exceedingly difficult to purify the oxide of copper. But a slight impurity, by the admixture of any sulphur-compound, may render the result perfectly useless, as frequently from 12 to 20 grms. of the oxide must be employed. For, assuming that we have 15 grms. of oxide of copper in the combustion-tube, which contain $\frac{1}{1000}$ sulphur, and 0·5 grm. of the substance to be burnt, the 15 grms. of oxide of copper consequently contain 0·015 grm. sulphur, which, calculated for 0·5 substance, produces an error of 3 per cent. in the amount of sulphur.

Fuming nitric acid, nitromuriatic acid, or muriatic acid with chlorate of potash, cannot well be employed with volatile compounds, as the latter evaporate readily on the requisite heat being applied, and escape the action of the oxidizing agent. Unger observed, in the analysis of crude soda, that the sulphur compounds contained in it could not be oxidized with fuming nitric acid without loss of sulphur.

The following method, adapted for all cases, but especially for the analysis of volatile compounds, has furnished me with very satisfactory results:—

1 equiv. bichromate of potash, which has been purified by recrystallization, is dissolved with 2 equivs. of pure carbonate of potash or soda in water, and the liquid evaporated to dryness; in this way a lemon-coloured mass, consisting of 1 equiv. neutral chromate of potash, and $\frac{1}{2}$ an equiv. of carbonate of potash or soda, is obtained. It is powdered, and in order to remove the last portions of water, exposed to a good red heat in a Hessian crucible, and then filled while hot into a glass tube sealed at one end and drawn out somewhat at the other, so that when wanted the chromate of potash can be conveniently poured into the combustion-tube without loss. This precaution is necessary with the use of the carbonate of potash, as it absorbs water from the air, and on being subsequently heated in the combustion-tube, again parts with it, and easily cracks the tubes. After the chromate of potash has cooled in the above-mentioned corked glass tube, a layer of it, of about 3 to 4 inches in length, is poured into a combustion-tube such as is used in organic analysis, the substance then added, and then again a few inches of the mixture of chromate and carbonate of potash. When the substance to be analysed is a solid, it is mixed intimately with the chromate of potash in the combustion-tube by means of a wire twisted at one end like a corkscrew. When this is done, the empty portion of the combustion-tube is filled with a mixture of chromate and carbonate of potash, placed in a furnace, and heated as for an organic analysis. When the whole is incandescent, oxygen is disengaged from a small retort, and passed in a slow current over the red-hot mixture for about half an hour or an hour. When cold,

the tube is cleansed of adherent ash, cut into several pieces over a sheet of paper, these placed in a beaker, and so much water poured over them as may be necessary to dissolve the calcined mass. The liquid thus obtained is made strongly acid with muriatic acid, some alcohol added to reduce the chromic acid, and heated gently upon the sand-bath until the solution has assumed the colour of the perchloride of chromium. The liquid is now filtered from the insoluble oxide of chromium obtained by the combustion, washed at first with water containing some muriatic acid, afterwards with alcohol, and then dried. The filtered green solution, which contains nearly the whole amount of the sulphuric acid, is placed aside for a time; and the oxide of chrome collected on the filter, which always most tenaciously retains a small quantity, frequently 1 to 2 per cent., of sulphuric acid in the form of a basic salt, is dried. The oxide of chrome is then emptied into a platinum crucible, the filter burnt, and its ashes added to the chrome compound in the platinum crucible. The latter is now mixed intimately by means of a glass rod with a mixture of 1 part chlorate of potash and 2 parts carbonate of potash, and then heated to redness until the whole of the oxide of chrome is converted into chromate of potash. The fused mass is dissolved in dilute muriatic acid, the chromic acid reduced by alcohol, and the liquid added to that previously obtained. The united solutions are now heated to boiling, the sulphuric acid precipitated with chloride of barium, and the amount of sulphur calculated from the sulphate of baryta.

In the determinations made by me, I connected the combustion-tube with a potash-apparatus filled with a dilute solution of chemically-pure potash, in order to condense any sulphur compounds not retained in the former; but in no one instance had a trace of a sulphur compound escaped from the combustion-tube.

The carbonate of soda which is obtained from the chemists as chemically pure, very often contains from 0·001 to 0·002 hyposulphite of soda. Determinations made with such material give from 3 to 4 per cent. too much. The following determinations were made according to the above-described method:—

0·154 grm. pure sulphur gave 1·12 grm. sulphate of baryta.

0·223 grm. of sulphur gave 1·618 grm. of sulphate of baryta.

Sulphur	99·76	99·50

0·256 grm. xanthamide, which is resolved at 302° F. into mercaptan and cyanuric acid, gave 0·563 grm. sulphate of baryta.

	Found.	Calculated.
Sulphur	30·2	30·4

0·174 grm. of a compound having the formula $C^{12} H^{10} O^8 S^3$, gave 0·320 grm. sulphate of baryta.

	Found.	Calculated.
Sulphur	25·28	24·76

Liebig's *Annalen*, October 1850.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Colouring Matter of Fustic (Mor tinctoria).

By Dr. R. WAGNER.

[Concluded from p. 5.]

Moritannic Acid.—As previously stated, I have applied this name to the peculiar tannic acid which exists along with the morine in fustic, and is contained in the liquid from which the morine-lime has been deposited. The larger proportion of the deposits in the centre of the blocks of the *Morus tinctoria* consists of this acid. To obtain this deposit in greater quantity, the blocks are split lengthways, and the layers of substance worked out with a chisel. As the body is easily obtained in this manner, I did not attempt to prepare it by evaporating the decoction of the fustic. The above deposit occurs in dirty yellow pieces, which here and there are of a flesh colour, have a reddish-brown fracture, and are laminar-crystalline; they are frequently half an inch thick. They dissolve almost entirely in alcohol, æther and boiling water; a great portion of the moritannic acid again separates from the boiling aqueous solution on cooling. When a fragment of the crude substance, as it occurs in the wood, is heated upon platinum foil, it becomes black and melts to a fluid, which changes into an exceedingly bulky cinder, difficult to burn, and which, after combustion, leaves but a mere trace of ash (0·6 per cent.).

The crude acid is purified in the following manner:—It is first repeatedly crystallized from water, and then, in order to separate a reddish resinous substance which adheres to it, it is dissolved in a larger quantity of boiling water to which a few drops of hydrochloric acid have been added, and the turbid solution filtered. When the solution no longer becomes turbid, it is set aside. After long standing, the moritannic acid separates from the liquid as a bright yellow crystalline powder, which appears under the microscope to consist of slightly yellow transparent prisms.

The taste of moritannic acid is sweetish, astringent, not unlike that of the inner peel of the walnut. This acid dissolves sparingly in cold, but very readily in boiling water. The solutions are yellow, and have a decidedly acid reaction. 1 part acid dissolves in 6·4 parts water at 68° F., and in 2·14 parts at 212°. It is also readily

soluble in alcohol, wood-spirit and æther. The concentrated ætherial solution is yellowish-brown by transmitted light, and greenish by reflected light. Moritannic acid is not soluble in oil of turpentine, naphtha and fat oils; from the aqueous, alcoholic and ætherial solutions it again separates in the cold on spontaneous evaporation, for the greater part in a crystalline state.

Moritannic acid exhibits towards reagents some very remarkable properties, which distinguish it from all hitherto known tannic acids. Acids, excepting the oxidizing ones, as nitric and chromic acids, &c., have but a weak action upon it.

Concentrated sulphuric acid dissolves it in the cold with a yellow colour; by the careful addition of water, so that the liquor does not become heated, the moritannic acid is again separated from this solution with all its properties unaltered. On the application of heat, the liquid turns brown, and disengages sulphurous acid and an exceedingly strong smell of carbolic acid (hydrated oxide of phenyle). If the cold prepared solution be set aside for some days, a brick-red crystalline substance separates, which acquires a magnificent purple colour, scarcely inferior in beauty to that of murexide, by the merest trace of ammonia or a few puffs of tobacco. I shall return to this interesting substance and its relation to moritannic acid.

On ebullition with dilute hydrochloric acid, moritannic acid dissolves with a red colour; and after a few days the same brick-red substance separates from the solution as is formed in the action of sulphuric acid. Long-continued boiling with concentrated hydrochloric acid produces a complete decomposition of the moritannic acid, with deposition of a humus-like substance. In all these decompositions a strong odour of carbolic acid is perceptible. When boiled with dilute nitric acid, a brown resin, readily soluble in boiling alcohol, is formed; the solution filtered from the resin contains oxalic acid. A similar resinous substance is formed when moritannic acid is conveyed into a mixture of fuming nitric and sulphuric acids.

Chromic acid entirely decomposes the acid, with evolution of the above-mentioned odour.

Chlorine, passed into the aqueous solution of moritannic acid, furnishes brown resinous products. A solution of isinglass, and also softened animal membrane, precipitates the moritannic acid completely from its solution. The liquid filtered from the yellowish-brown precipitate gives with salts of iron merely a faint greenish colour, but no precipitate

Moritannic acid is partly precipitated from its aqueous solution by tartar-emetic; the precipitate, which consists of moritannate of the oxide of antimony, is yellowish-brown; the filtered liquid is yellowish; salts of iron strike a green colour with it. This liquid contains a compound of moritannic acid with bitartrate of potash.

Nitrate of silver produces no precipitate; but on the addition of a few drops of ammonia and boiling, the oxide of silver is immediately reduced; carbonate of silver is reduced in the cold. The sulphate of the magnetic oxide of iron gives a greenish-black pre-

cipitate, which dissolves in acetic acid with a yellowish-brown colour. Sulphate of copper gives a yellowish-brown precipitate. When heated with acetate of copper, hydrated protoxide of copper separates after a time. Neutral acetate of lead furnishes a precipitate of the colour of the chromate of lead, which dissolves in boiling water, and separates in distinct lemon-coloured crystals on cooling. Perchloride of gold is reduced in the cold. Chloride of platinum gives, after a time, a yellow flocculent precipitate. Perchloride of mercury furnishes no precipitate; but on the addition of potash and the application of heat, separation of protoxide of mercury results. Protochloride of tin gives a reddish-yellow precipitate. Alum alone gives no precipitate; on the addition of carbonate of potash, a lemon-coloured lack is produced. Bichromate of potash furnishes, on the application of heat, a bulky reddish-brown precipitate; the neutral chromate of potash, a reddish-brown solution.

Muriate of quinine precipitates moritannic acid from its aqueous solution; the precipitate is bright yellow; the filtered liquid is colourless, and is neither precipitated by salts of iron nor by potash.

Caustic and carbonate alkalies dissolve moritannic acid with a dark yellow colour; the solution soon acquires in the air a brown, and finally a brownish-black colour. Moritannic acid expels the carbonic acid from the alkaline and earthy carbonates on ebullition, but not in the cold.

Disengagement of hydrocyanic acid results on boiling it with ferrocyanide of potassium, and a yellowish-brown flocculent precipitate forms in the liquid. When boiled with ferridcyanide of potassium, there is also a copious disengagement of hydrocyanic acid, and after long ebullition a precipitate of the proto- and percyanide of iron is formed. Cyanide of potassium is equally decomposed on ebullition.

The aqueous solution of moritannic acid is not precipitated by sulphuric, hydrochloric, phosphoric and arsenic acids; its behaviour is consequently exactly the reverse of quercitannic acid. Dissolved with boracic acid in boiling water, it furnishes on cooling a gelatinous mass, consisting of extremely thin yellow laminæ; in this respect it behaves like quercitannic acid*.

Behaviour of Moritannic Acid at an elevated Temperature.—The acid, dried at 212°, heated in a bath of metal, melts at 392°, gives off at 482° a very acid water, and is converted into a liquid brownish-black substance; complete decomposition takes place above 518°, when a large amount of carbonic acid is disengaged. When moritannic acid is heated in a retort to 572°, carbonic acid is likewise disengaged, and a brownish oily liquid passes over, from which, after some time, colourless prismatic crystals are deposited; the crystals may be freed from adherent oily liquid by pressure between blotting-paper. The liquid obtained in the dry distillation of moritannic acid dissolves in water, alcohol, and in part in æther. It is coloured dark green by persalts of iron. The crystals constitute a new acid, which, from its analogous origin with pyrogallic acid, I shall call *pyromoritannic acid*. There is also formed a large quan-

* See Löwig's Chem. d. organischen Verbindungen, vol. i. p. 703.

tity of an uncrystallizable oil, which dissolves in water, and possesses all the properties of the hydrate of the oxide of phenyle (spirole, carbolic acid). A splint of resinous wood, moistened with hydrochloric acid, immediately acquires a splendid purple-red colour on being dipped in this liquid. Runge states, it is true, that the hydrate of the oxide of phenyle should produce a blue colour, and assumes that pyrrhole (the picoline of Anderson) may be distinguished from the hydrated oxide of phenyle by the purple-red colouring; as however I operated with pure moritannic acid, there could be no production of the nitrogenous pyrrhole. It is rather to be supposed that the reactions ascribed by Runge to the hydrated oxide of phenyle and pyrrhole are not characteristic. Nevertheless, in the present case, the presence of the hydrate of the oxide of phenyle is indicated by the production of the purple-red colour, as the similar kreosote produces no colour under the same conditions when perfectly freed from carbolic acid. I must moreover observe, with respect to the reaction described by Runge, that it not only takes place on employing pine, fir and larch wood, but also with any other soft and half-hard wood; and not only with muriatic acid, but likewise with dilute sulphuric, nitric, arsenic and phosphoric acids, but not with the organic acids.

Distinction of Moritannic Acid from Quercitannic and the other Tannic Acids.—That moritannic acid belongs to the large class of the tannic acids is evident from its behaviour towards animal membrane, salts of iron, and its astringent taste. Adopting the old division of the tannic acids, according to their deportment towards salts of the peroxide of iron, moritannic acid belongs to those that strike a green colour with iron, although this difference is by no means general, as a decoction of gall-apples, mixed with vinegar or tartaric acid, likewise precipitates the persalts of iron of a green colour, whilst the tannic acids of the cinchona-bark and of catechu precipitate persalts of iron blue when they contain a small quantity of a free alkali. In the same manner, a compound of moritannic acid with oxide of lead turns blue on the addition of persulphate of iron.

Moritannic acid differs from the acids of catechu, kino, galls, and the caffeotannic acid described by Rochleder, chiefly in the following particulars:—*It is the only crystallizable tannic acid yet known*; *it is a yellow pigment*; *its lead-salt is soluble in water*. It differs from quercitannic acid principally in its not being precipitated from its aqueous solutions by acids, and from the tannic acids of kino, coffee and catechu by its behaviour towards tartar-emetic.

Analysis of Moritannic Acid.—The material which served for analysis was crystallized from water several times, and left on combustion not a trace of ash; it furnished—

Carbon.....	55·55	55·16	55·18	54·94	18	= 108	55·102
Hydrogen	4·53	4·58	4·50	4·26	8	8	4·081
Oxygen	..	..	..	..	10	80	40·817

I employed for the determination of the atomic weight the combinations of moritannic acid with oxide of lead and lime, without

however being able to discover with certainty from the results obtained the equivalent of the acid. As evident from the analysis of the lead-salt described below, the atomic weight of the acid in it was always 140 in the most different preparations. The numbers obtained in the analysis of the lime-salt do not accord with this. The simplest expression obtained by elementary analysis for the composition of the acid is $C^9 H^4 O^5$. This however must be doubled, from analogy of moritannic acid with ordinary tannic acid and catechu-tannic acid. I was unable to determine the amount of water in moritannic acid in the usual way by means of hydrated oxide of lead, as it exerts a decomposing influence on the acid.

If we admit preliminarily the formula of the ordinary tannic acid as correct, then a gap in the series of the tannic acids is filled up by the discovery of moritannic acid. Quercitannic, moritannic and catechu-tannic acids are different oxides of the radical $C^{18} H^8$, for—

$C^{18} H^8 + 12O$, quercitannic acid.
$C^{18} H^8 + 10O$, moritannic acid.
$C^{18} H^8 + 8O$, catechu-tannic acid.

According to Wetherill, the tannic acid of the gall-nuts is isomeric with gallic acid dried at 212°*. If we adopt for the latter the formula $C^7 H^3 O^5$, then the composition of tannic acid is expressed by $C^{14} H^6 O^{10}$. If we allow those reagents, under whose influence the metamorphosis of tannic into gallic acid takes place, to act upon tannic acid, crystallized gallic acid is formed, with the assimilation of 1 equiv. of water.

According to Mulder†, the formula of tannic acid is $C^{28} H^9 O^{17}$, HO; and it is also, according to that chemist, isomeric with gallic acid. This view of Wetherill and Mulder is greatly supported by the fact, that morine and moritannic acid, which stand in the same relation to each other as gallic to tannic acid, catechuic to catechu-tannic acid, are likewise isomeric. On comparing the results I obtained in the analysis of morine and moritannic acid, and the numbers which Berzelius found in the analysis of catechu-tannic acid, and Zwenger in the analysis of catechuic acid, it will be found that the results agree as closely as possible for substances the absolute purity of which must always remain somewhat doubtful‡. The admission of isomerism in these bodies appears therefore to be justified. Adopting Wetherill and Mulder's formula for tannic acid as a general one, all the tannic acids hitherto analysed, and most of their derivatives, may be brought into *one* series with 14 or with 28 equivs. of carbon, whilst at present we must admit two series, one with

* Chem. Gaz., vol. v. p. 483. † Chem. Gaz., vol. viii. p. 41.

‡ Berzelius obtained, in the analysis of catechu-tannic acid, $C^{15} H^8 O^8$, and Zwenger, in the analysis of catechuic acid, the following numbers:—

	Catechu-tannic acid.	Catechuic acid.
Carbon	60·00	59·871
Hydrogen	4·44	4·886
Oxygen	35·56	35·244

18 equivs. carbon (quercitannic, moritannic, catechu-tannic acids), and one with 14 (caffeotannic acid). If we attempt to incorporate the moritannic acid in the series with 14 or 28 equivs. of carbon, then morine stands in the same atomic relation to moritannic acid as gallic acid to the ordinary tannic acid. Moritannic acid and morine would then obtain the following formulæ, $C^{14}H^{6}O^{8}$, or $C^{28}H^{12}O^{16}$, which require 54·54 C, 3·89 H, and 41·57 O per cent.

According to this formula, moritannic acid is isomeric or polymeric with the boheic acid of Rochleder*. The connexion between moritannic acid, but still more between morine and morindine, $C^{28}H^{16}O^{16}$†, and gentianine, $C^{14}H^{9}O^{5}$‡, is very evident. These substances may possibly be the gallic acids of isomeric, hitherto unknown tannic acids.

Admitting the isomerism of the tannic acids with the corresponding gallic acids, and adopting Rochleder's caffeotannic acid ($C^{14}H^{8}O^{7} = C^{14}H^{6}O^{5} + 2HO$) as a starting-point, we have the following series of bodies, which may be viewed as different oxides of the common radical $C^{14}H^{6}$:—

$C^{14}H^{6}+5O$ = caffeotannic acid.
$C^{14}H^{6}+6O$ = catechu-tannic acid, catechuic acid, kinic acid.
$C^{14}H^{6}+7O$ = viridic acid.
$C^{14}H^{6}+8O$ = moritannic acid, morine, boheic acid.
$C^{14}H^{6}+9O$ = metagallic acid.
$C^{14}H^{6}+10O$ = tannic acid, gallic acid.

In the present paper I retain the expression $C^{18}H^{8}O^{10}$ for the composition of morine and moritannic acid. I shall in a future communication, which will treat of the products of decomposition and the constitution of these two bodies, enter into a fuller discussion of the formulæ of the tannic acids in general.

Salts of Moritannic Acid.

The behaviour of moritannic acid towards bases has been already noticed in describing the action of different reagents towards this acid. I have prepared and analysed the neutral and basic lead salts, the lime salt, the peroxide of iron salt and the quinine compound. I did not succeed in obtaining salts of the alkalies of constant composition, and the baryta salt did not furnish accordant results.

Moritannate of Lead.—As already stated, neutral acetate of lead produces in an aqueous solution of pure moritannic acid a yellow precipitate, which dissolves in boiling water, and separates partly from the solution on cooling in the form of a lemon-coloured crystalline powder. The liquid filtered from this powder deposits, after standing for some time, some very bulky yellow flakes of variable composition. It sometimes happens, when the solution of lead salt has been allowed to boil for some length of time, that no crystals separate from the filtered liquid, but only these flakes. When hydrated oxide of lead is boiled with a solution of moritannic acid and the liquid filtered hot, the lead salt is also deposited in the crystal-

* Chem. Gaz., vol. vi. p. 72. † *Ibid.*, vol. vi. p. 313. ‡ *Ibid.*, vol. v. p. 446.

line state; but the supernatant liquid is brown, so that probably a portion of the moritannic acid is decomposed by the hydrated oxide of lead. This lead salt has the peculiarity of being coloured dark brown by even dilute nitric acid. The moritannic acid is separated by sulphuretted hydrogen from the lead salt in an apparently unaltered state; but I have not examined it. The lead salt, dried at 212°, gave the following results:—44·49, 44·19, 44·28 per cent. oxide of lead; and on analysis—

Carbon.....	32·01	54 =	324	32·17
Hydrogen.....	2·17	21	21	2·08
Oxygen	21·65	27	216	21·45
Oxide of lead	44·27	4	446	44·30

leading to the formula $3C^{18}H^{7}O^{9}+4PbO$.

If we admit that moritannic acid is, like quercitannic acid, a tribasic acid, $C^{18}H^{5}O^{7}, 3HO$, then the rational formula of the analysed lead salt will be—

$$C^{18}H^{5}O^{7}\left\{\begin{matrix}2PbO\\HO\end{matrix}\right\}+2C^{18}H^{5}O^{7}\left\{\begin{matrix}PbO\\2HO\end{matrix}\right\}+HO.$$

The Basic Lead Salt was prepared by precipitating a boiling solution of moritannic acid with basic acetate of lead. After drying, it forms a chrome-yellow amorphous powder, nearly insoluble in water. It furnished 57·5 and 56·9 per cent. oxide of lead. The formula $C^{18}H^{5}O^{7}, 2PbO, HO$ would require 55·5, and the less probable formula $C^{18}H^{5}O^{7}, 2PbO$, 56·9 per cent. of oxide of lead.

Moritannate of Lime.—This compound is prepared by boiling an aqueous solution of moritannic acid with pure carbonate of lime until disengagement of carbonic acid ceases; the liquid is filtered hot; after several hours, yellowish-brown flakes separate, which are collected upon a filter and dissolved in alcohol. The filtered solution is poured into from 8 to 10 times the quantity of distilled water, when the moritannate of lime separates in yellow microscopic crystals, which are collected upon a filter, pressed between blotting-paper, and dried at 212°. It furnished 7·708 and 7·18 per cent. of lime; the formula $2C^{18}H^{5}O^{7}+CaO, HO+2HO$ requires 7·12 per cent. of lime.

This compound is so much like the morine-lime compound existing in the fustic, that the two could not be distinguished by analysis, appearance, behaviour to acids, alkalies and solvents in general, and by their deportment on platinum foil; but the perchloride of iron furnishes us with the means of distinguishing these substances. An aqueous solution of morine-lime strikes a red colour with perchloride of iron, whilst the moritannate of lead gives a blackish-green precipitate.

Moritannate of the Peroxide of Iron.—On mixing perchloride of iron with moritannic acid (the latter not being in excess), a blackish-green precipitate is produced, which, after washing and drying, forms a grayish-green mass. Dried at 212°, it gave 13·2 per cent. of peroxide of iron; the formula $Fe^{2}O^{3}+3C^{18}H^{5}O^{7}$ would require

13·8 per cent. No value however can be placed on this formula, as a portion of the peroxide might have been reduced to protoxide.

Moritannate of Quinine.—This compound was prepared by precipitating a solution of moritannate of lime with one of hydrochlorate of quinine. The substance, dried at 212°, is of a yellow colour, not crystalline, somewhat soluble in water and readily in alcohol. It furnished—

Carbon	63·40	74 =	444	63·25
Hydrogen.....	5·47	38	38	5·41
Nitrogen	3·89	2	28	3·98
Oxygen.....	27·24	24	192	27·36

Admitting Laurent's formula for anhydrous quinine, $C^{38}H^{22}N^2O^4$, this compound may be expressed by $C^{38}H^{22}N^2O^4+2C^{18}H^5O^7$, 3HO; but if we adopt the earlier formula for quinine, $C^{20}H^{12}NO^2$, it then becomes $C^{20}H^{12}NO^2+C^{18}H^5O^7$, 3HO, which requires 63·7 per cent. of carbon and 5·59 of hydrogen.

Some Observations relative to the exhausted Fustic, and dyeing with Fustic in general.

The fustic which has been exhausted by repeated digestion with boiling water, imparts a dark reddish-yellow colour to a dilute solution of potash; acids precipitate an impure brown-coloured pectic acid from this solution; the supernatant liquid is yellow, and still contains a considerable quantity of the colouring substances. It appears as if only a portion of the colouring substances could be extracted by water from the fustic, as in the case of madder. Gülich states, in his work on bleaching and dyeing, that, after completely exhausting the fustic, some of the colouring particles still remain behind, which are of a resinous nature, and may be extracted by alcohol and alkalies. Some experiments which I made to set the colouring matters free, by treating the exhausted fustic with hydrochloric or sulphuric acid, and so producing substances corresponding to *garancine* or *garanceux*, led to no results. Fustic which had been exhausted with water gave, on being boiled with milk of lime, a yellowish-brown filtrate, which dyed mordanted stuffs of a very intense yellow. Hydrochloric acid precipitates no pectic acid from this liquid. To turn to account the whole of the colouring matter contained in fustic, it might perhaps be advisable to extract the wood exhausted by water by further ebullition with milk of lime. Lime is certainly preferable to potash or soda, because the pectic acid, dissolved at the same time by the latter bases, interferes with the beauty of the colours.

Exhausted fustic exhibits a peculiar behaviour towards acids. When the wood, which has been completely exhausted with water and solution of potash, so that the liquid no longer appears coloured, is moistened with hydrochloric or dilute sulphuric acid, it turns cochineal-red; acetic acid colours it brick-red.

With reference to the dyeing capacity of fustic, it is stated in several works, and among others in Dumas's Manual and Bancroft's

'Art of Dyeing,' that fustic contains a large amount of tannin, and that the presence of this substance in the wool treated with it produces roughness and brittleness, which is very injurious to the spinning of it. Chaptal has advised, in order to overcome this difficulty, to add waste skin to the decoctions of fustic in order to precipitate the tannin. It results however from my investigations, that the tannic acid contained in fustic constitutes the principal colouring matter; and to precipitate the moritannic acid from the fustic-bath would, in other words, be to destroy much of the dyeing power of the decoction. In some few cases, where it is desirable to obtain a more beautiful and fuller yellow from fustic, approaching closely to that from weld and quercitron, Chaptal's process might perhaps be applied.

Experiments made for the purpose of testing the applicability of the colouring matters of fustic in the new process of Broquette*, which consists in the use of *caseogomme* (caseine-lime), gave very unsatisfactory results. A piece of cotton stuff, mordanted with caseine-ammonia, gave, on treatment with decoction of fustic, a very beautiful yellow colour, which however soon passed into a dirty brown. The lime compound does not act much better. This deportment is explained from the properties of the colouring matters of fustic being very soon altered by free alkalies. It might perhaps be worth the trouble to make some experiments as to the applicability of the caseine-magnesia.

The following conclusions may be drawn from the preceding paper:—

1. Fustic contains two yellow colouring principles, *morine* and *moritannic acid*. The first exists in the wood in combination with lime.

2. The two substances are isomeric, and have the formula $C^{18} H^8 O^{10}$.

3. Morine behaves towards bases as a weak acid, enters into combination with them, and has in these compounds the formula $C^{18} H^5 O^7$.

4. Moritannic acid is, like quercitannic acid, tribasic, and its formula may be written $C^{18} H^5 O^7 + 3HO$.

5. As regards composition, moritannic acid is situated between quercitannic, $C^{18} H^8 O^{12}$, and catechu-tannic acid, $C^{18} H^8 O^8$.

6. It is the first known crystallizable tannic acid, and differs from all the other tannic acids hitherto examined by its composition and its behaviour towards persalts of iron, tartar-emetic and salts of lead.—*Journ. für Prakt. Chem.*, li. p. 82.

Presence of Uric Acid in the Blood in Health and Disease.

By Dr. GARROD.

The author has made the interesting discovery that uric acid exists in the blood, both in gout and even in the healthy state. The form in which it is contained in that liquid is that of urate of soda.

* Chem. Gaz., vol. viii. p. 384.

The author's process was as follows:—1000 grs. of the serum were evaporated to dryness in thin layers in the water-bath. The residue was powdered and treated with rectified spirit, boiled for about 10 or 15 minutes, again treated in the same way, and the spirituous solutions preserved for examination. After again washing with spirit, the dried serum was exhausted with boiling water, the operation being repeated two or three times, and the watery solutions mixed. On evaporating a small quantity of this liquid with the addition of nitric acid, and holding the residue over the vapour of ammonia, distinct evidence of the existence of uric acid was afforded by the production of the beautiful tint of murexide. The aqueous solution was then evaporated until it became slightly thick, and when cool was acidulated with muriatic acid. On standing for some hours, crystals of uric acid were deposited; these were collected, washed with alcohol, and weighed. When the above process was followed without the addition of the acid, the concentrated aqueous solution was found to deposit crystals of urate of soda in the form of tufts of needles.

In four cases of gout, the quantity of uric acid in 1000 grs. of serum was found to be as follows:—

I.	II.	III.	IV
0·050 gr.	0·025 gr.	0·045 gr.	0·030 gr.

The author arrives at the following conclusions regarding the relation of uric acid to gout:—

1. The blood in gout contains uric acid in the form of urate of soda, which, as has been shown, can be obtained from it in a crystalline state.

2. The uric acid is diminished in the urine immediately before the gouty paroxysm. This was shown by the examination of the urine of the patient from whom the blood (IV.) had been removed. For several days, at the commencement of the gouty attack, no uric acid could be detected in it, although on the third day a trace could be discovered by the murexide test, and a few crystals were deposited, whilst the blood during this time gave abundant evidence of its presence. When the attack had subsided, the uric acid was present in the urine in its normal quantity.

In the urine of the patient (II.) when the attack was passing off, the uric acid amounted to 0·050 gr. only; hence not more than one-twelfth of the natural quantity. The same fact was proved to occur in other cases.

3. In patients subject to chronic gout with tophaceous deposits, the uric acid is always present in the blood and deficient in the urine, both absolutely and relatively to the other organic matters; and the chalk-like deposits appear to depend on an action in and around the joints, &c. vicarious of the "uric-acid-excreting" function of the kidneys.

4. The blood in gout sometimes yields a small portion of urea (no albumen being present in the urine), as shown by the crystallization with nitric acid.

The quantity of uric acid in the blood of healthy persons, or at

least those suffering from slight headache or other trifling affections, was found to amount, per 1000 grs. of serum, in one case to 0·007 gr., in another to a trace only; in two patients suffering from slight paralysis and an ill-conditioned habit of body, to 0·010 gr. No trace could be found in the blood of the sheep nor in that of the pigeon; the urine of the former contains no uric acid, whilst that of the latter consists entirely of urate of ammonia.

The author moreover found, in several examinations of perfectly healthy blood, that uric acid was invariably present.

It appears, then, from these experiments, that in health (or tolerable health) uric acid can be detected in the blood of the human subject. It appears also, that when the function of excretion is very perfectly performed, no trace can be detected, although, as in the case with birds, the amount of uric acid formed in the system is very large.

In regard to rheumatism, the author found the blood to contain no more uric acid than in health; and no urea can be detected in 1000 grs. of serum.

In cases of albuminuria, uric acid is always present in the blood; the quantity however varying. When the functions of the kidneys are much impaired, it exists in quantities almost as great as in gout; in other cases its amount is small, but it usually exceeds that found in ordinary blood. Urea always exists in large quantities in this blood, as is well known, and no relation is found between the amounts of urea and uric acid. In the examination of the blood in albuminuria, some of the colouring matter of the urine seemed to be thrown down with the uric acid in all cases. The author regards the quantities of uric acid found by him in the blood in his earlier experiments as rather below the true amounts. He recommends that the crystals should not be collected until forty-eight hours have elapsed. The author suggests whether, in doubtful cases, it might not be possible to determine as to the presence of gout or rheumatism from an examination of the blood.—*Trans. Med. Chir. Soc. of London*, Feb. 1848.

On a Method of determining the Effective Hardness of Emery, with Observations on its Chemical Composition. By J. Lawrence Smith.

Fragments are broken from the piece to be examined, and crushed in a diamond mortar with two or three blows of a hammer, then thrown into a sieve (the one employed had four hundred holes to the square centimetre), the portion passing through is collected, and that remaining on the sieve is again placed in the mortar and two or three blows given, then thrown into the sieve; the operation is repeated until all the emery has passed through the sieve. The object of giving but two or three blows at a time is to avoid crushing any of the emery to too fine a powder.

Thus pulverized, it is intimately mixed, and a certain portion of it is weighed (as I operated with a balance sensible to a milligramme,

the quantity used never exceeded a gramme). To test the effective hardness of this, a circular piece of glass about 4 inches in diameter and a small agate mortar are used. The glass is first weighed, and placed on a piece of glazed paper; the pulverized emery is then thrown on it little by little, at each time rubbing it against the glass with the bottom of the agate mortar.

The emery is brushed off the glass from time to time with a feather, and when all the emery has been made to pass once over the glass, it is collected from the paper and made to pass through the same operation, which is repeated three or four times. The glass is then weighed, after which it is subjected to the same operation as before, the emery being by this time reduced to an impalpable powder. This series of operations is continued until by repeated weighing the loss sustained by the glass is reduced to a few milligrammes. The total loss in the glass is then noted; and when all the specimens of emery are submitted to this operation under the same circumstances, we get an exact idea of their relative hardness.

The blue sapphire of Ceylon was pulverized and experimented with in this way; it furnished me with a unit of comparison by which to compare the results obtained. This operation is long but certain, and for the harder varieties of emery it is necessary to repeat the rubbing six or seven times, and it requires nearly two hours for completion.

The results that I have obtained are interesting, and have furnished me with the means of forming conclusions that I could not have otherwise come at.

Glass and agate have not been chosen for this experiment without a certain object, as experiments were first made with two pieces of agate, with two pieces of glass, and with metal and glass. The agates were found too hard, as they crushed the emery without producing hardly any abrasive effect; the others were found not to crush the emery sufficiently, making the experiment tedious and long. With the glass and agate we have a hard substance which crushes the emery, and in a certain space of time reduces it to such an impalpable state that it has no longer any sensible effect on the glass, and on the other hand the glass is soft enough to lose during this time sufficient of its substance to allow of accurate comparative results. In the employment of this method in the arts, it would not be necessary to go to the sapphire for a standard of comparison; any good emery would answer the purpose quite as well.

It must be understood that this method of coming at the abrasive effects of emery does not furnish the mineralogical hardness of this substance, by which we understand the hardness of any individual particle, as evinced by its effect on a substance of less hardness, without regard to the molecular structure of the mineral. Two minerals possessing the same hardness but differing in structure, one being friable and the other resisting, will be found very different in their abrasive effects; for instance, break a piece of quartz in two; subject one of the pieces to a white heat, and after cooling compare the two by rubbing the point against some hard substance; both

will be found to scratch equally well. Then try the two in a state of powder, by rubbing them between two pieces of glass that have been weighed, and the difference of their abrasive effects will be found very great, because the one subjected to the fire is exceedingly friable, and becomes readily crushed to an impalpable powder. This fact is eminently true with reference to emery, many specimens of which containing the same amount of corundum differ somewhat in their *effective hardness*, owing to the more or less compact structure of the corundum.

By the method with the agate and glass I have found the best emery capable of wearing away about one-half its weight of the glass (that used was the common French window-glass). The sapphire under the same circumstances wears away more than four-fifths of its weight. A tabular view of the results will be given a little further on.

Chemical Composition.—This substance consisting of a mixture of corundum and oxide of iron in various proportions, it is easy to see what its composition must be. Yet the chemical examination of this mineral, taken in connexion with other properties, is not devoid of interest.

For the purpose of analysis, the emery was reduced to a state of powder, in the manner alluded to in speaking of its hardness, with a diamond mortar and sieve. This powder was dried for twenty-four hours over sulphuric acid; a gramme was then weighed in a small platinum crucible of about one-fourth of a cubic inch in capacity, fitted with a cover that adapted itself well to it; this small crucible was placed in another of earth, and the space between the two filled with pulverized quartz, which also covered the smaller one to the depth of half an inch. Common sand was not used, because during the heating some particles might adhere to the platinum crucible by a semifusion; nor was powdered charcoal employed, because it protected the mineral no better than the pulverized quartz from contact with the air; at the same time a little risk was run in decomposing a small amount of the iron.

Thus arranged, the crucibles were heated to a bright red for from thirty minutes to one hour. After cooling, the platinum crucible was carefully withdrawn and weighed. The loss furnished me with the amount of water in the emery.

It requires a continued red heat to drive out all the water, a circumstance which is true for a number of minerals, particularly for those containing a large amount of alumina, as diaspore and some micas.

The powder, of which the water has been estimated, was next submitted to levigation in a large agate mortar placed on a surface of glazed paper; and when completed, it was carefully detached from the mortar, placed in a platinum capsule, heated gently to drive off any hygrometric moisture, and weighed; the increase of weight furnished the amount of silica taken from the mortar.

The levigation of 1 grm. was accomplished in two operations, each requiring about twenty minutes; and by using a mortar of

convenient size and the extremity of a feather or a small brush, it is possible to lose but an insensible quantity of the mineral, and to estimate with sufficient precision the amount of silica abraded from the mortar.

Another method by which I accomplished the levigation in some of the analyses, was in a steel mortar of the same form as the agate mortar; and when completed, the powder was placed in a glass with nitric acid diluted with 30 times its weight of water, and left in it for one hour, agitating it occasionally. The iron taken from the mortar was dissolved, and no part of the mineral attacked. The next thing was to filter, and continue the analysis with the substance thus freed from the iron of the mortar, without any second weighing.

Of these two methods I prefer to employ the first for the emery, as it is more expeditious, and almost, if not quite as exact as the second. There are however occasions in which the steel mortar should be resorted to.

The substance once reduced to an impalpable powder, it was necessary to render it *completely* soluble, and my researches to arrive at this were long and tedious. In trying the various known methods, the most successful was found to be that with a mixture of carbonate of soda and caustic soda heated to whiteness for one hour; nevertheless I could not obtain a complete decomposition. The decomposition might probably be completed if the levigation was made more thoroughly; but it is easy to understand, that with a large number of analyses of the same substance to make, it was a desideratum on my part not to consume the best part of the day in the levigation of a single gramme; particularly as I did not wish to confide this operation to another, as much care was required to lose nothing during the levigation. Mixed with carbonate of baryta, and heated in a forge, the decomposition of the mineral was far from being complete; the same may be said for the treatment with the caustic alkalies in a silver crucible.

The bisulphate of potash decomposes it almost entirely by a single operation, but unfortunately a double salt of potash and alumina is formed, which is almost insoluble in water or in the acids, and it is only by a solution of potash that it is first decomposed, and afterwards redissolved. I will not stop to detail all the disadvantages attending this method, but will at once speak of the method which gave me very easily the most accurate results.

It is by means of the bisulphate of soda that all my analyses of emery, of corundum, and of several aluminates, were made. I believe that I am the first who has shown the great advantage of using this double salt in the decomposition of certain substances insoluble in the acids; and very probably it will replace in most cases the use of the bisulphate of potash in analytical chemistry. At present, all the advantages that may arise from the substitution of the soda for the potash salt cannot be mentioned; all that I will say is, that the former, in giving a decomposition at least as complete as the latter, furnishes a melted mass quite soluble in water; and in the future

operations of the analyses there is no embarrassment from a deposit of alum.

The bisulphate of soda was prepared by adding an excess of pure sulphuric acid to the pure carbonate or neutral sulphate of soda, and heating it in a capsule until all the water had been expelled and sufficient of the acid to allow of the mass becoming solid on cooling. That obtained in commerce is not sufficiently pure.

The pulverized emery is placed in a large platinum crucible with 6 or 8 times its weight of bisulphate of soda, and the mixture is heated over a lamp in the same manner and with the same precautions as are employed when using the bisulphate of potash. From fifteen to thirty minutes suffice for the operation. The mass is allowed to cool, and water with a few drops of sulphuric acid are added to it, and the whole heated, when it soon dissolves with the exception of a little silica, that renders the solution milky, and a small quantity of undecomposed mineral, that is readily detected by rubbing a glass rod against the bottom of the capsule. The liquid is now filtered, and the filter is washed once with a little water; then with its contents it is placed in a platinum crucible, burnt completely, and the residue is heated with a little bisulphate of soda, which completes the decomposition; and when treated with water and a drop or two of sulphuric acid, all except the silica is dissolved. The liquid which passes the filter in this case is added to the first, and the analysis continued. The silica obtained is diminished by the quantity taken up from the mortar in order to arrive at what is actually contained in the mineral. The filtered solution is heated with a little nitric acid to convert all the protoxide of iron into peroxide, then treated with an excess of caustic soda and a little carbonate of the same alkali; this redissolves the alumina first precipitated, and thus separates it from the oxide of iron and a trace of lime. The iron and lime are separated in the ordinary way; the alkaline solution of alumina was acidulated, and the alumina precipitated with carbonate of ammonia.

Thus analysed, the emery from different places gave the following results:—

No.	Localities.	Effective hardness. Sapphire 100.	Specific gravity.	Chemical composition.					
				Water.	Alumina.	Oxide of iron.	Lime.	Silica.	Total.
1	Kulah	57	4·28	1·90	63·50	33·25	0·92	1·61	101·18
2	Samos	56	3·98	2·10	70·10	22·21	0·62	4·00	99·03
3	Nicaria	56	3·75	2·53	71·06	20·32	1·40	4·12	99·43
4	Kulah	53	4·02	2·36	63·00	30·12	0·50	2·36	98·34
5	Gumuch	47	3·82	3·11	77·82	8·62	1·80	8·13	99·48
6	Naxos	46	3·75	4·72	68·53	21·10	0·86	3·10	101·31
7	Nicaria	46	3·74	3·10	75·12	13·06	0·72	6·88	98·88
8	Naxos	44	3·87	5·47	69·46	19·08	2·81	2·41	99·23
9	Gumuch	42	4·31	5·62	60·10	33·20	0·48	1·80	101·20
10	Kulah	40	3·89	2·00	61·05	27·15	1·30	9·63	101·13

I ought to mention that the analysis afforded other substances in small quantities in some of the emeries; as titanic acid, oxide of

manganese, oxide of zirconium and sulphur (existing in pyrites); but these substances are unimportant in the composition of emery, and are in such minute quantities, that it is necessary to operate on a considerable quantity of the mineral to obtain satisfactory results concerning them.

The analyses marked 6 and 8 were made by decomposing the emery as it came from the sieve, without pulverization in the agate mortar. It was by accident that it occurred, and I was not aware of the neglect until it was fused with the bisulphate of soda; but not wishing to lose the analysis, the operations were continued as in the other cases, only using a little more of the bisulphate in the second decomposition; and, somewhat to my surprise, the decomposition was quite as perfect as in the other cases. I had nearly completed all my analyses in the manner detailed when this fact became known, so that I have but these two cases to report.

The water which was found in the emery comes from the corundum. A very minute quantity of what has been estimated as water might be a little oxygen lost by the oligiste which is sometimes found in emery. Those emeries which contain the least water, everything else alike, are the hardest, as instanced by that from Kulah, notwithstanding the quantity of iron it contains. The silica existing in emery is most often in combination with alumina or the oxide of iron, or with both; for this reason we must not always regard the quantity of alumina as an indication of the quantity of corundum in the emery.—Silliman's *Journal*, November 1850.

On the Composition of Minium. *By* Prof. Mulder.

The composition of minium may be expressed by two different formulæ. According to Dumas, this oxide contains Pb^3O^4, and should be viewed as a combination of 2PbO with PbO^2. M. Winckelblech, on the contrary, considers that minium contains sesquioxide of lead combined with protoxide, $Pb^3O^4 = PbO + Pb^2O^3$. This sesquioxide, Pb^2O^3, was prepared by M. Winckelblech by adding hypochlorite of soda to a solution of oxide of lead in potash.

M. Houlton Labillardière examined a red crystallized compound prepared in a minium furnace, the composition of which was expressed by the formula—

$$Pb^4O^5 = 2PbO + Pb^2O^3, \text{ or } 3PbO + PbO^2.$$

Lastly, M. Longchamps examined a kind of minium which contained—

$$Pb^6O^7 = 4PbO + Pb^2O^3, \text{ or } 5PbO + PbO^2.$$

From what precedes, it is seen that the composition is variable. M. Mulder has analysed seven different kinds of minium, either by calcining the oxide and determining the loss in weight, or by treating it with nitric acid and weighing the residue of peroxide. The first method of analysis does not furnish accurate results, for minium always contains a small quantity of carbonic acid, which is disengaged with the oxygen. From the experiments of M. Mulder, it results that the majority of miniums have the composition—

$Pb^4O^5 = 2PbO + Pb^2O^3$, or $3PbO + PbO^2$,

which is the same as that assigned to them by Houlton Labillardière. —*Journ. für Prakt. Chem.*, l. 438.

Occurrence of Crystallized Oxide of Chromium in Furnaces for the Manufacture of Chromate of Potash. By W. P. Blake.

Crystals of the sesquioxide of chromium have been obtained in small quantities by Wöhler, by passing the vapour of chlorochromic acid through a tube heated to redness.

The crystals which I have examined with the following results were obtained from a furnace which had been long in operation for the production of chromate of potash from the mineral chromic iron. A portion of the furnace having been taken down for repairs, I found small but exceedingly brilliant crystals lining the cracks and fissures between the fire-bricks, and disseminated throughout their substance. They resembled crystals of specular iron, but a blow-pipe examination and qualitative analysis proved them to be the sesquioxide of chromium.

The crystals are of the hexagonal system, and are flat six- or twelve-sided tables or scales. The breadth of the largest is $1\frac{1}{2}$ line, but they are seldom over a line broad, and usually much smaller. In some of the specimens the crystals are grouped in rosettes of great beauty.

The crystals have the hardness of sapphire, equal to 9 on the scale of Mohs; lustre, metallic; colour, black; opake, except in thin plates, which are green by transmitted light. The powder of the crystals is dark green.

The specimens were taken from and between the bricks which had constituted the floor of the furnace. The furnace had been in operation for more than a year, and kept at a temperature above redness. As it needed repairs, the fires were drawn, it was allowed to cool undisturbed for ten days, and when the bricks were taken out they were still too hot to be taken in the hand.

The mass of the bricks and the portions on which the sesquioxide has crystallized is charged with soluble yellow chromate of potash, and in many or all of the specimens the green colour of the uncrystallized oxide can be seen.

My frequent daily examinations of the furnaces in operation made me familiar with the condition in which the contents were at different times; and considering the facts before stated, I account for the production of the crystals in the following way:—

When the furnace, newly constructed or lined with fire-brick, is fired and charged with alkali and chrome ore, much of the fused chromate of potash formed is absorbed by the porous bricks, and I observed that it had penetrated through three or four courses of bricks and mortar.

After the furnace has been long in operation, the bricks become saturated and vitrified to a certain depth; and the floor and sides of the furnace become incrusted with a vitreous coating, which is con-

stantly increasing. The parts more remote from the fire are consequently better protected from changes and variations of temperature, and are exempt from the inroads of more fused material.

The chromate of potash is thus kept for a long time at a uniform high temperature, and gradually losing its potash from volatilization, the chromic acid (CrO^3) in combination with it loses oxygen, becomes sesquioxide ($Cr^2 O^3$), and crystallizes.—Silliman's *Journal*, November 1850.

On the Presence of Bile in the Blood. By Dr. C. Enderlin.

The colouring matter of the bile has long since been shown positively to occur in the blood, both when in a healthy and diseased state, by the characteristic reaction of nitric acid. M. Enderlin states that he has satisfactorily detected bilic acid in both human blood and that of the ox. His method of proceeding was as follows:—

A pound of blood, taken from a woman in the eighth month of pregnancy, was evaporated to perfect dryness in the water-bath; the finely-pulverized residue was exhausted with æther to remove the fatty matters, and then, at the ordinary temperature, with strong alcohol; the alcoholic solution evaporated, and the residue treated with absolute alcohol. The reaction of the solution was somewhat strongly alkaline, its taste bitter, and it possessed the odour of bile. A few drops evaporated upon platinum-foil left an ash which strongly effervesced with an acid. It was evaporated to dryness, exhausted with water, and the following experiments made with the aqueous extract:—

a. A small quantity was treated with sulphuric acid. A milky troubling was produced, and on gentle digestion yellowish-brown resinous drops separated. *b.* Another portion was concentrated in a watch-glass upon the water-bath, the residue placed upon platinum-foil, a trace of sulphuric acid added, and a gentle heat applied. The azure-blue colour, subsequently passing into a blood-red, was produced, which is considered a test for the detection of the presence of biliary matters. On the further application of heat, the mass became brownish, exhibited the appearance of old bile, and possessed a most distinct odour of bile. *c.* The remainder of the aqueous solution was precipitated with basic acetate of lead, the resinous precipitate boiled with alcohol, and the solution evaporated to dryness. The lead-compound was decomposed with carbonate of soda, the filtrate evaporated, and the dry residue exhausted with absolute alcohol; the yellowish-brown extract again evaporated, and the residue treated with water. The aqueous solution exhibited the reactions of bilate of soda with mineral acids and lead-salts; it possessed an alkaline reaction, and when heated with a trace of sulphuric acid, exhibited the above-mentioned beautiful colours. The greater part of the aqueous solution was boiled with strong muriatic acid. It gave off a distinct odour of bile, and after some time dirty brown drops separated, which on cooling became solid, and dissolved in alcohol. The alcoholic solution exerted an acid reaction

(the drops were washed with hot water), tasted bitter, decomposed carbonate of soda with effervescence, and was rendered milky by water. These are the characters of choloidic acid.

M. Enderlin regards these experiments as showing beyond doubt that this blood contained bile. The presence of bile in the blood of an ox was detected by the same means in an even more satisfactory manner. M. Enderlin states that he has detected Gmelin's cholic acid, taurine and choloidic acid in human intestinal evacuations in bilious diarrhœa. On two occasions the cholic acid was obtained in stellate prisms by Strecker's method. In most instances the biliary matters were recognized by their reaction on ebullition with sulphuric acid and with muriatic acid (formation of cholic acid). He was unable to detect unaltered bile.

M. Enderlin considers the bile to serve another purpose in addition to that of respiration, viz. he regards it as the source of hæmatine, &c.—Liebig's *Annalen*, vol. lxxv. p. 167.

On the Equivalent of Iron. *By* E. Maumené.

The number representing the equivalent of iron has been raised, in accordance with some recent analyses, from 339·23 to 350. The author having had occasion to examine some very pure iron, made some experiments to confirm this. The metal was dissolved in weak aqua regia, the oxide precipitated by ammonia, collected upon a filter, and, after having been washed with hot water and dried at 230° F., calcined in a platinum crucible. The mean of six analyses made in this way gave 350·01.—*Journ. de Pharm.*, Dec. 8, 1850.

ANALYTICAL CHEMISTRY.

On the Estimation of Iodine in Organic Substances by means of Chloroform. *By* M. Rabourdin.

The detection of iodine by means of starch paste leaves nothing to be desired as regards sensitiveness; but this is no longer the case when the quantity of iodine in organic substances has to be determined. Chloroform may be advantageously placed by the side of starch as a test for traces of iodine, for by means of this reagent its presence may be detected in a liquid containing less than one hundred thousandth of its weight. If we take 10 grms. of a liquid containing one hundred thousandth of its weight of iodide of potassium, add to this liquid 2 drops of nitric acid, 15 to 20 drops of sulphuric acid and 1 grm. of chloroform, the latter after agitation acquires a very distinct violet tint.

I have endeavoured to turn to account this remarkable property which chloroform possesses of removing from water the iodine which it is capable of holding in solution in the free state and of acquiring a violet colour, in order to estimate approximatively

the iodine in organic substances, and especially in cod-liver oil, so largely employed in medicine at the present day.

I take 50 grms. of cod-liver oil, which I mix by agitation in a phial with 5 grms. of caustic potash dissolved in 15 grms. of distilled water, and heat this mixture in a large iron spoon, in order to destroy the whole of the organic matter; the cinder is exhausted with distilled water, to remove the soluble portion; as little water as possible should be employed; the liquid is filtered; 10 drops of nitric acid and of concentrated sulphuric acid are added, taking care to cool the mixture; 4 grms. of chloroform are then poured into it, and the whole well shaken. After a time the chloroform is deposited, coloured violet; the supernatant liquid may be decanted, and the chloroform solution be washed with water without depriving it of its colour.

On the other hand, a normal liquor is prepared containing 1 centigrm. of iodide of potassium in 100 grms. of distilled water, so that 10 grms. represent 1 milligrm. of iodide. We now take 10 grms. of this solution, 20 drops of sulphuric acid and 4 grms. of chloroform; by agitation, a colouring is obtained, which is compared with the tint furnished by the cod-liver oil; in general it is necessary to add 1, 2 or 3 grms. of the normal solution, in order for the tint to be of the same depth.

I have examined the three principal kinds of cod-liver oil which are found in commerce:—

1. Dark mahogany colour, called brown in commerce.
2. Amber-coloured, called blonde in commerce.
3. Colourless, called white or English in commerce.

Each kind was examined three times, operating, as above stated, upon 50 grms. To obtain a tint of the same depth as that furnished by 50 grms. of the brown oil, I employed 14 grms. of the normal solution, or 0·0014 of iodide of potassium, and only 12 grms. of the same solution for the two other kinds of oil. These three oils contain therefore very nearly the same proportion of iodine, which would be 1 milligrm. for 50 grms., admitting that no loss occurs in the incineration.

I have likewise ascertained by experiment, that chloroform removes completely any free iodine from an aqueous solution. I saturated 500 grms. of water with pure iodine; after having filtered the solution, I agitated it three different times with 15 grms. of chloroform; the third time the chloroform was in every instance scarcely coloured.

A very small quantity of iodine colours pure chloroform a very beautiful violet, perfectly similar to the tint of the vapour of iodine; but if the chloroform is mixed with sulphuric æther, even in very small quantity, instead of the violet colour, it has more the colour of red wine, or even of caramel, if there be any quantity of æther present. This character may assist in detecting the sophistication of chloroform by æther.—*Comptes Rendus*, Dec. 2, 1850.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Constitution of Codeine and its Products of Decomposition.

By Thomas Anderson, M.D.*

It will be unnecessary for me to premise any observations regarding the history of codeine and its discovery, which are sufficiently well known, further than to refer to the analyses and formulæ given for it by the different chemists by whom it has been examined. Codeine has been analysed by its discoverer, Robiquet, and by Couerbe, Regnault, Will, Gregory and Gerhardt. All the analyses of these observers I have brought together in the following table, in which however the per-centage results are not those found in the original papers, but have been calculated from the analytical numbers according to the new equivalent of carbon†:—

Anhydrous Codeine.

	Robiquet.	Couerbe.		Regnault.		Gregory.	Will.
Carbon....	70·363	71·59	72·10	73·31	72·93	73·18	73·27
Hydrogen..	7·585	7·12	7·17	7·19	7·23	7·23	7·25
Nitrogen ..	5·353	5·23	..	4·89	4·89	4·82	
Oxygen ..	16·699	16·06	..	14·61	14·95	14·77	

Crystallized Codeine.

	Gerhardt.	
Carbon	67·77	67·87
Hydrogen	7·59	7·33
Nitrogen		
Oxygen		

From these analyses, four different formulæ have been deduced. Two of these, however, those of Robiquet and Couerbe, do not require particular mention, as they were unsupported by any accurate determination of the atomic weight of the substance, and are now certainly known not to represent its true constitution. That which has been hitherto most generally adopted by chemists is the one founded by Regnault upon his analysis, and represents codeine as $C^{35}H^{20}NO^5$, and the crystallized base as $C^{35}H^{20}NO^5+2HO$; the calculation of which gives—

* We are indebted to the kindness of the Author for a copy of this paper, from the Transactions of the Royal Society of Edinburgh, vol. xx. Part I.—W. F.

† In the case of Robiquet and Will's analyses, the details of the experiment are not given. I have therefore been obliged to convert the per-centage of carbon into carbonic acid, according to the old equivalent of carbon, and recalculate it into carbon according to the new equivalent.

	Anhydrous.	Crystallized.
Carbon	73·94	69·53
Hydrogen	7·04	7·28
Nitrogen	4·92	4·63
Oxygen	14·10	18·50

The analyses of Will and Gregory have usually been quoted in confirmation of this formula. It is clear however that the agreement between the calculated and experimental results is by no means satisfactory, either in them or in Regnault's own results, the highest amount obtained for the carbon being 0·63 per cent. below the calculation, while the lowest differs by more than 1 per cent., and the mean of the whole four gives 0·77 too little carbon, involving a loss which could not possibly have occurred in carefully-made analyses.

Partly on account of this difference, and partly guided by his views regarding the divisibility of formulæ, Gerhardt was induced to doubt the exactitude of Regnault's formula, which presents three different deviations from his law; the number of equivalents of carbon and of oxygen being uneven, and the sum of the equivalents of hydrogen and nitrogen also indivisible by two. He therefore repeated its analysis, using the crystallized codeine, and obtained the results contained in the table, and deduced from them the formula $C^{36}H^{21}NO^{6}$ for the anhydrous base, which gives the calculated results—

	Anhydrous.	Crystallized.
Carbon	72·24	68·13
Hydrogen	7·02	7·25
Nitrogen	4·68	4·41
Oxygen	16·06	20·11

and tallies extremely well with his analysis. This formula has however been again called in question by Dollfus*, who has endeavoured to determine the constitution and atomic weight of the alkaloids by the analysis of their hydrosulphocyanates, and obtained from the codeine salt of that acid, results agreeing with the formula $C^{34}H^{19}NO^{5}$. Considering the known accuracy of Regnault, and of the chemists by whom his formula has been confirmed, I considered it an essential preliminary to my investigation to repeat its analysis with all possible care, so as to determine which of the two represents its true constitution.

1. *Preparation and Analysis of Codeine.*

I have little to add to the information we already possess regarding the preparation of codeine. I have obtained it, as usual, from the mother-liquor from which morphia has been precipitated by ammonia. As the codeine forms only from a sixteenth to a thirtieth of the morphia, it is of course mixed in this fluid with a corresponding quantity of muriate of ammonia, which must be decomposed by potash in order to obtain it. Much advantage is gained however by first evaporating the fluid to crystallization, and expressing the crystals deposited, as in this way the greater part of the muriate of ammonia, which is the

* Chem. Gaz., vol. vi. p. 202.

more soluble salt of the two, is left in solution; and by repeating the crystallization many times, it may be entirely removed, and crystals obtained which are pure hydrochlorate of codeine. For the preparation of codeine however it would be worse than useless to carry the process thus far, as the solubility of the hydrochlorates of codeine and ammonia differs so little, that much of the former salt would be lost; but by carrying it a certain length, the greater part of the sal-ammoniac may be separated without any material loss of codeine, and the subsequent steps of the process much facilitated. The crystals so obtained being dissolved in boiling water, strong solution of caustic potash is added in excess, when codeine is in part precipitated as an oil, which by and by concretes into a solid mass, and is partly deposited in crystals as the solution cools. By evaporating the fluid, another crop of crystals is obtained; and finally, when the mother-liquor has been concentrated to a very small bulk, it becomes filled on cooling with long silky needles of morphia, which has been retained in solution by the excess of potash. A certain quantity of morphia appears always to remain in solution along with the codeine; at least I have found it in all the mother-liquors I have examined, although its quantity appears to vary considerably. Its presence in this solution has been observed before, and it has been stated that it exists in the form of a double salt with codeine; this however is not consistent with my own experience; at least the salt separated from the muriate of ammonia by successive crystallizations contained no morphia, but, as has been already stated, was pure hydrochlorate of codeine.

The crystals of codeine, precipitated by potash in the manner described, are always more or less coloured. They are purified by solution in hydrochloric acid, boiling with animal charcoal and re-precipitation with a slight excess of potash, and the precipitate obtained finally dissolved in æther, to separate any morphia which may adhere to it. For this purpose hydrous æther is best adapted; and it ought to be free from alcohol, as if any be present the æther evaporates, and a syrupy fluid is left behind, which refuses to crystallize. When the æther is anhydrous, it dissolves codeine with much greater difficulty, and by evaporation small crystals are deposited, which are anhydrous.

The codeine employed for analysis was dried at 212°. The three first were made with codeine crystallized from hydrous æther, which lost 2 equivs. of water at 212°. The last was anhydrous codeine in small colourless crystals. The nitrogen was determined by Will and Varrentrapp's method:—

	I.	II.	III.	IV.
Carbon	71·91	72·02	72·09	72·09
Hydrogen	7·05	7·04	7·14	7·16
Nitrogen	4·41	4·60	4·50	
Oxygen	16·63	16·34	16·27	

These results confirm, in all respects, the formula $C^{36}H^{21}NO^6$, the calculated results of which are given in a former page. The

determination of the atomic weight of codeine by the analysis of its platinum salt presented considerable difficulties, and at first gave extremely discordant results, the per-centage of platinum varying from 18·51 to 20·30. I found however that by precipitating in the cold, a salt was obtained, to be afterwards described, which gave sufficiently uniform results. This salt, dried at 212°, retained an equivalent of water. It gave, as the mean of seven experiments, the details of which will be afterwards given, 19·25 per cent. of platinum, while the calculation, according to the above formula, requires 19·19 per cent. These determinations leave no doubt as to the formula of codeine, and they are fully confirmed by the result of the analyses of the substances to be described in the sequel of this paper.

Codeine crystallized from water or hydrous æther is obtained in crystals, often of considerable size, belonging to the right-prismatic system, and presenting a considerable number of modifications. These crystals contain 2 equivs. of water of crystallization, as determined by this experiment:—

7·126 grs. crystallized codeine lost at 212°, 0·454 = 5·66 per cent. water. The calculated result gives 5·67.

Codeine is an extremely powerful base, rapidly restoring the blue of reddened litmus, and precipitating oxides of lead, copper, iron, cobalt, nickel, and other metals, from their solutions. It is precipitated by potash from its salts, and is generally stated to be insoluble in that alkali; but this is true only of very highly concentrated solutions, as a considerable quantity of strong potash may be added to a saturated solution of codeine in water without producing precipitation; and even when a very large amount of potash is added, a certain quantity of the base is still retained in solution. Codeine is soluble in ammonia, but not more so than in water. 100 parts of a moderately-strong solution of ammonia dissolved, at 60°, 1·46 part of codeine; and according to Robiquet, 100 parts of water at 59° dissolve 1·26 part. Contrary to what is usually stated, I have found that codeine is precipitated from all its salts by ammonia; it does not however fall immediately, but is slowly deposited in small transparent crystals.

II. *Salts of Codeine.*

Hydrochlorate of Codeine.—This salt is readily obtained by saturating hot dilute hydrochloric acid with pure codeine. If the solution has been sufficiently concentrated, it becomes nearly solid on cooling; but if more dilute, the salt is deposited in radiated groups of short needles, which under the microscope are found to be four-sided prisms terminated by dihedral summits. It is never obtained in large crystals, even when considerable quantities are crystallized. These crystals are soluble in 20 times their weight of water at 60°, and in less than their weight of water at 212°. Codeine is precipitated from the saturated cold solution immediately by potash; ammonia gives no precipitate, but after some time colourless crystals are deposited. The crystallized hydrochlorate of codeine contains

water of crystallization, and presents some curious anomalies in its relations to that fluid. When dried in the air, it retains 4 equivs. of water, 1 of which escapes at 212°, but the remaining 3 are only expelled at 250°, and at the same time the salt loses acid and acquires an alkaline reaction. It would appear also that, under certain circumstances, the salt is deposited in anhydrous crystals, as one analysis of it, dried at 212°, gave numbers corresponding to the anhydrous salt. I could not however again succeed in obtaining it in this condition; but many analyses were made which gave results lying between those of the anhydrous and crystallized salts, and the only means of explaining the discrepancy is by supposing that the two sorts of crystals had been deposited simultaneously and in variable proportions. The following is the analysis of the salt dried at 212°:—

Carbon	59·68	36	= 216	59·38
Hydrogen	7·08	25	25	6·89
Nitrogen	..	1	14	3·86
Oxygen	..	9	72	19·88
Chlorine	..	1	35·5	9·79

10·735 grs. of the salt lost, at 212°, 0·31 gr. of water = 2·88 per cent. 1 equiv. of water gives by calculation 2·42 per cent. The formula of the air-dried salt is therefore $C^{36}\ H^{21}\ NO^6\ HCl + 4HO$.

The anhydrous salt gave the following results. Of these, No. I. is the salt obtained by direct crystallization from the morphia mother-liquor, No. II. is that which was got anhydrous at 212°, and No. III is a portion dried at 250°; it had become strongly alkaline, which accounts for the excess of carbon obtained:—

	I.	II.	III.			
Carbon	64·37	64·56	64·93	36	= 216	64·38
Hydrogen	6·83	6·74	6·71	22	22	6·55
Nitrogen	..	..	..	1	14	4·17
Oxygen	..	..	..	6	48	14·32
Chlorine	..	..	..	1	35·5	10·58

These results correspond to the formula $C^{36}\ H^{21}\ NO^6\ HCl$.

Hydriodate of Codeine is obtained by dissolving codeine in hot hydriodic acid, and allowing the solution to cool. It is deposited in long slender needles, which fill the whole fluid if it has been sufficiently concentrated. It is of rather sparing solubility in cold water, requiring about 60 times its weight, but is much more soluble in boiling water. Its saturated cold solution is precipitated by ammonia on standing. No difficulty was experienced in its analysis:—

	I.	II.			
Carbon	48·16	48·64	36	= 216	48·60
Hydrogen	5·69	5·70	24	24	5·40
Nitrogen	..	..	1	14	3·15
Oxygen	..	..	8	64	14·45
Iodine	..	28·22	1	126·36	28·40

The formula of the salt, dried at 212°, is therefore $C^{36}H^{21}NO^6HI + 2HO$.

Sulphate of Codeine crystallizes in radiated groups of long needles, or by spontaneous evaporation in flattened four-sided prisms. It requires for solution 30 times its weight of cold water, but it is very soluble in the heat. When pure, it is neutral to test-paper; but it is very liable to retain a small quantity of acid, which can be got rid of by repeated crystallizations. The first analysis was made with the salt which had been only once crystallized, and has therefore given an excess of sulphuric acid.

Analysis of the salt, dried at 212°, gave the following results:—

	I.	II.			
Carbon.....	61·44	61·64	36 =	216	62·07
Hydrogen	6·52	6·50	22	22	6·39
Nitrogen	..	..	1	14	4·03
Oxygen	..	..	7	56	16·03
Sulphuric acid....	11·75	11·54	3	40	11·49

27·13 grs. of the crystallized salt lost, at 212°, 3·068 grs. of water = 11·30 per cent. This corresponds to 5 equivs. of water, the calculated result for which is 11·45.

The formula of the crystallized salt is therefore $C^{36}H^{21}NO^6HO\,SO^3 + 5HO$.

Nitrate of Codeine is obtained by slowly adding nitric acid, of spec. grav. 1·060, to powdered codeine, an excess of nitric acid being carefully avoided, as the base is rapidly decomposed by it with the formation of a product of substitution to be afterwards described. The nitrate is readily soluble in boiling water, and is deposited on cooling in small prismatic crystals. Heated on platinum, it melts, and on cooling concretes into a brown resinous mass; at a higher temperature, it is rapidly decomposed, leaving a bulky cinder, difficult of incineration:—

Carbon	59·40	36 =	216	59·66
Hydrogen.....	6·54	22	22	6·07
Nitrogen	..	2	28	7·73
Oxygen.....	..	12	96	26·54

These results correspond with the formula $C^{36}H^{21}NO^6HO\,NO^5$.

Phosphate of Codeine.—Several phosphates of codeine appear to exist, but I have only examined that which is obtained by saturating tribasic phosphoric acid with codeine in powder. In this way a fluid is obtained, which, when concentrated to a small bulk, refuses to crystallize, but from which crystals are immediately precipitated by the addition of strong spirit. The salt is thus obtained in small scales, or in short thick prisms. It is readily soluble in water, and cannot be obtained in crystals from the solution. Its analysis gave the following results, corresponding with the formula $C^{36}H^{21}NO^6HO\,2HO\,PO^5$:—

Carbon	54·25	36 =	216	54·27
Hydrogen.....	6·49	24	24	6·03
Nitrogen	..	1	14	3·52
Oxygen.....	..	9	72	18·09
Phosphoric acid ..	..	3	72	18·09

6·911 grs. of the crystallized salt lost, at 212°, 0·434 gr. of water =6·27 per cent. 3 equivs. of water correspond to 6·35 per cent., and the formula of the crystallized salt is consequently $C^{36}\,H^{21}\,NO^{6}$ HO 2HO PO + 3HO.

Oxalate of Codeine.—This salt is deposited, on cooling its saturated hot solution, in short prisms, and sometimes in scales. It requires 30 times its weight of water at 60° for solution, and about half its weight at 212°. Heated to 212°, it loses water of crystallization; at 250° it becomes brown, and at a higher temperature it is entirely decomposed:—

Carbon	66·19	38 =	228	66·28
Hydrogen.....	6·60	22	22	6·39
Nitrogen	..	1	14	4·07
Oxygen.....	..	10	80	23·26

10·050 grs. of the crystallized oxalate lost, at 212°, 0·704 gr. of water =7·00 per cent., corresponding to 3 equivs. of water, which requires 7·27 per cent. The formula of the crystallized salt is therefore $C^{36}\,H^{21}\,NO^{6}$ HO $C^{2}\,O^{3}$ + 3HO.

Hydrosulphocyanate of Codeine.—This salt has been already examined by Dollfus; but I have prepared it, and repeated the analysis, with results differing somewhat from those obtained by him. It is readily obtained by mixing solutions of hydrochlorate of codeine and of sulphocyanide of potassium, and is slowly deposited in beautiful radiated needles. The numbers furnished by analysis correspond with the formula $C^{36}\,H^{21}\,NO^{6}\,HC^{2}\,NS^{2}$, as is shown by the following per-centage calculation, to which I have added the results obtained by Dollfus:—

	Dollfus.	Anderson.			
Carbon.....	62·30	63·20	38 =	228	63·68
Hydrogen	6·13	6·38	22	22	6·14
Nitrogen	..	..	2	28	7·82
Oxygen	..	..	6	48	13·43
Sulphur	..	9·04	2	32	8·93

11·613 grs. of the crystallized salt, dried at 212°, lost 0·288 gr. of water =2·47 per cent., corresponding to 1 equiv. of water, the calculation of which gives 2·45 per cent.

In the analysis of Dollfus, there is manifestly a loss of carbon, as the results are quite incompatible with those of the base and its other salts. In the same paper Dollfus has also determined the amount of sulphocyanogen by precipitation with silver, and the results obtained agree better with the formula given above than with his own.

Chloride of Platinum and Codeine.—When bichloride of platinum is added to a moderately-concentrated solution of hydrochlorate of

codeine, a pale yellow pulverulent precipitate is deposited. If this be allowed to stand for some time in the solution, or still better, if it be collected on a filter and kept moist, it begins to change in its appearance, specks of darker colour appear in it, and it is gradually converted into a mass of crystalline grains of an orange-yellow colour. The fluid which filters off deposits on standing a small quantity of larger grains. The change which takes place in this manner is not always complete, and the granular crystals are often mixed with unchanged yellow powder. When the chloride of platinum is added to a more dilute solution of hydrochlorate of codeine, precipitation does not take place immediately, but in a short time the salt is deposited in minute tufts of silky needles. The salt is soluble in boiling water, and is deposited on cooling partly in grains, partly as a powder. By this process however it is partially changed, and I have ascertained that by ebullition, with excess of chloride of platinum, it is completely decomposed. I have not as yet however followed up this observation. I at first attempted to purify the salt by solution in water and alcohol, in which it is also soluble; and a number of analyses were made, which gave extremely contradictory results; but by precipitation in the cold, and without excess of platinum, sufficiently uniform results were obtained.

When dried at 212°, the salt retains an equivalent of water, which is expelled at 250°, but not without occasioning partial decomposition of the substance, which evolves acid, and acquires a brownish colour. The following are the results of analysis:—

	I.	II.	III.	IV.	V.	VI.	VII.
Carbon	41·70	42·36	41·70	41·80	42·00		
Hydrogen ..	4·49	4·62	5·01	4·72	4·97		
Nitrogen ..							
Oxygen							
Chlorine....							
Platinum ..	19·31	19·14	18·92	19·32	18·98	19·08	19·00

These analyses correspond with the formula $C^{36}H^{21}NO^6HCl + PtCl^2 + HO$, of which the following is the calculated result compared with the mean of experiment:—

Carbon	41·91	36 =	216	42·07
Hydrogen.....	4·76	23	23	4·47
Nitrogen	..	1	14	2·72
Oxygen.....	..	7	56	10·94
Chlorine	..	3	106·5	20·61
Platinum	19·25	1	98·7	19·19

The air-dried salt, when dried at 212°, lost 5·11 to 5·20 per cent. This corresponds to 3 equivs. of water, the calculated result for which gives 4·99 per cent. The crystallized salt is therefore represented by the formula $C^{36}H^{21}NO^6HCl + PtCl^2 + 4HO$.

Codeine forms many other crystallizable salts, none of which however have been examined. The chromate is easily obtained in fine yellow needles. With solution of bichloride of mercury, codeine

gives a white precipitate, soluble in boiling water and alcohol, and deposited on cooling in stellated groups of crystals. With chloride of palladium a yellow precipitate is obtained, which is decomposed by boiling, with separation of metallic palladium. Tartrate and hydrocyanate of codeine are uncrystallizable.

[To be continued.]

On a new Substance isomeric with Starch. *By* J. Gottlieb.

Standing waters sometimes become filled with an enormous multitude of a green infusorium, *Euglena viridis*, which is everywhere common. Mixed with minute Algæ, or their remains, they form on the water in which they live green frothy layers, which in warm weather, when removed, reappear with remarkable rapidity. These animals contain, both in their living state as well as long after their death, a large number of minute granules, which, with their green colour, and especially when, as frequently happens, they are contracted into a spherical shape, impart to them a great resemblance to a vegetable cell filled with very minute granules of starch. When the animals are crushed under the microscope, these make their escape without exhibiting the least connexion with each other or any previous attachment to the envelope of the animal. These granules are not coloured blue by iodine, and are therefore not identical with starch; but they have much in common and the same composition, on which account the author has assigned to the substance the name of *paramylon*.

The author collected a large number of *Euglenæ* at a spot where they occurred almost free from other infusoria. A part of the fresh animals was exhausted with æther and alcohol, in which media the green colouring substance dissolved. After complete exhaustion with æther and alcohol, the animals present a tolerably brilliant violet colour. The violet colouring substance was removed by a boiling mixture of alcohol and muriatic acid, in which it is readily soluble. The *Euglenæ* were then left as a yellowish-white mass.

In this treatment, most of the envelopes of the animals burst, when the granules escape; and we have then under the microscope a mixture of the envelopes, granules and uninjured animalcules. The separation of the granules from the membranes was effected by pouring the mixture suspended in water upon very fine clean cotton tissue, through which the water passed turbid, and after standing for some time, deposited the granules in the form of a dazzling white sediment. This operation was several times repeated; there was left on the cloth a mixture of cases and granules with sand. The granules, thus purified and dried at 212°, gave on analysis—

Carbon	44·87	..	12 = 72		44·44
Hydrogen	6·46	6·28	10	10	6·18
Oxygen	48·67	..	10	80	49·38

Consequently the granular substance, which was certainly not perfectly free from membrane, had exactly the composition of starch.

This however is still more evident from the following analyses of the pure granular substance, which was obtained by digesting the granules at the ordinary temperature with dilute caustic potash. The substance then dissolves, leaving a residue of sand and pieces of membrane. On mixing the alkaline fluid with dilute muriatic acid, the substance separated in the form of a transparent, opalescent, gelatinous, tumescent body. The removal of the chloride of potassium and the muriatic acid is effected very slowly by edulcoration, but completely. There is simultaneously formed a small quantity of a brown substance soluble in potash, from which it is in part precipitated by acids, and the presence of which, on drying the separated mass, is recognised by a brownish colour. It is removed by repeated treatment with potash and precipitation with a mixture of muriatic acid and alcohol, which takes up the colouring substance. The substance thus purified left no ash; dried at 212°, it furnished on analysis exactly the composition of starch, viz.

Carbon.....	44·28	44·12	44·25	12	=72	44·44
Hydrogen.....	6·27	6·34	6·31	10	10	6·18
Oxygen.....	49·45	49·54	49·44	10	80	49·38

Properties of Paramylon.—The granules in the unaltered form, as well as the substance obtained by means of potash, are wholly insoluble in water and dilute acids even on ebullition. A considerable quantity of paramylon, boiled for six days with dilute sulphuric acid, gave, on filtration and saturation with carbonate of lime, evaporation to dryness, and treatment with alcohol, a very small quantity of a brownish smeary mass, in which there was apparently a trace of sugar. Fresh diastase had no apparent effect upon paramylon under the most favourable conditions for the production of sugar; however, on boiling it with an excess of fuming muriatic acid, it is quickly dissolved, giving a brown-coloured solution, and may now be converted into fermentative sugar. On adding an equal volume of water to the liquid, evaporating to one-half, and adding oxide of silver to the residue as long as chloride of silver is formed, the filtered liquid leaves on evaporation a brown syrupy mass of a decidedly sweet taste, which behaves towards copper solution like grape-sugar, and when mixed with yeast and water, soon exhibits the appearances of vinous fermentation. Like starch, paramylon can be converted by a high temperature into a gummy substance. Heated to about 392° in an air-bath, it turns brown without melting, and then yields to water a body which is tasteless, and leaves on evaporation a gum-like substance insoluble in alcohol.

The dried paramylon, modified by potash, swells in water without acquiring that gelatinous state which it has when precipitated from a dilute alkaline solution. The unaltered granules are white, very much like wheat-starch, only much smaller, and readily deprived of water at 212°. The dried substance, purified by potash, &c., forms minute, irregular, transparent, slightly yellowish fragments, which are tenacious, but imperfectly reduced to powder, and only part with the whole of the adherent water after long exposure to 410°.

On being heated, both melt and burn with an odour like sugar; the cinder burns readily. They are insoluble in solution of ammonia, even when boiled with it. A concentrated alkaline solution deposits, on the addition of acidified alcohol, the substance in white flakes, which, after washing and drying, cannot be distinguished from the body precipitated from more dilute solutions. Saline solutions exert no action. As regards its indifference to various chemical agents, paramylon closely resembles cellulose.—Liebig's *Annalen*, lxxv. p. 51.

On the Chlorosulphuret of Antimony. *By* S. Cloez.

Most chemists admit at present the analogy which exists between the corresponding compounds of nitrogen, arsenic and antimony. The aggregate of the chemical properties of these bodies tends to unite them into a group which is certainly as natural as that formed by fluorine, chlorine, bromine and iodine. Nevertheless those who admit the ill-founded division of the simple bodies into metalloids and metals place antimony among the latter, whilst nitrogen, phosphorus and arsenic are ranged among the metalloids.

The fact which I am about to communicate tends to corroborate the opinion of those who classify these four bodies in the same group, and represent by similar formulæ the analogous compounds they form.

We are acquainted among the compounds of phosphorus with a liquid discovered by Sérullas, whose composition is represented by the formula $PCl^3 S^2$. The action of hydrosulphuric acid upon the perchloride of antimony furnishes an analogous product having the formula $SbCl^3 S^2$.

To obtain this substance, well-dried hydrosulphuric acid is passed slowly over the perchloride placed in a tubulated retort; the gas is wholly absorbed in the cold, with an elevation of temperature and a disengagement of hydrochloric acid; when the reaction is finished, the liquid perchloride is converted into a white crystalline solid mass, which I have analysed, and have found to possess the composition represented by the formula $SbCl^3 S^2$. The following equation explains the formation of this compound:—

$$SbCl^5 + 2(HS) = SbCl^3 S^2 + 2(HCl).$$

The chlorosulphuret of antimony fuses at a low temperature; heated beyond its melting-point, it is decomposed into sulphur and protochloride of antimony. It is not altered in dry air, but greedily absorbs the moisture of the atmosphere, becoming converted into a yellow liquid of an oily consistence, holding finely-divided sulphur in suspension. Water poured upon the chlorosulphuret of antimony immediately decomposes it, producing a copious white precipitate of oxychloride of antimony, mixed with small yellow glutinous masses of sulphur. Hydrochloric acid acts like water; when added in sufficient quantity, the oxychloride dissolves, and may thus be readily separated from the sulphur.

Aqueous solution of tartaric acid has a peculiar action upon it,

giving rise to an orange precipitate of sulphuret of antimony mixed with a certain quantity of oxide. This reaction is characteristic; it proves that the compound in question is not a mere mixture of sulphur and protochloride of antimony, but a true compound.

I hope to obtain the *sulphoxyantimoniates* by acting upon the chlorosulphuret of antimony with the alkaline bases, but have not yet succeeded in obtaining them in a pure state; I am certain they exist, but they are very unstable.—*Ann. de Chim. et de Phys.*, Nov. 1850.

On the Constitution of Coniine. By Dr. R. Wagner.

Three different formulæ have been advanced for coniine, viz.

$C^{16} H^{16} N$, by Ortigoza.
$C^{17} H^{17} N$, by Blyth.
$C^{16} H^{17} N$, by Gerhardt.

If we compare the numbers obtained by different chemists in the analysis of coniine, and of the platinum salt with those found by calculation from the formulæ, it will be seen that Gerhardt's formula is most probable. Hofmann, in his "Memoir on the Constitution of the Organic Bases," has rendered it probable that most of them are formed from ammonia by the substitution of 1, 2 or 3 equivs. of hydrogen. The formation of butyric acid by the oxidation of coniine, by atmospheric air, by the action of chloride of platinum, of chromate of potash and sulphuric acid, of nitric acid, &c.,

$$C^{16} H^{15} N + 4HO + 4O = 2(C^6 H^7) C^2 O^3 + HO + NH^3,$$

furnishes us with the means of ascertaining with tolerable certainty the constitution of coniine, based upon the ideas of Hofmann. Admitting in coniine the radical butyryle, $C^8 H^7$ (according to Kolbe, $C^6 H^7 C^2$), then coniine may be viewed as dibutyrylamine, *i. e.* as ammonia in which 2 equivs. hydrogen have been replaced by 2 equivs. butyryle, for

$$C^{16} H^{15} N = \left.\begin{matrix} C^8 H^7 \\ H \end{matrix}\right\} N.$$

According to this view, coniine would be an imidogen basis with an analogous composition to the diæthylamine of Hofmann, $C^4 H^5$, $C^4 H^5$, $H + N$. If this assumed formula of coniine is the rational one, then it might be possible to manufacture coniine. Just as Hofmann has expected to prepare the base acetylamine, $\left.\begin{matrix} C^4 H^3 \\ H \\ H \end{matrix}\right\} N$, from the bromide of acetyle, we may expect to obtain from the bromide of butyryle (procured from the butyric aldehyde of Guckelberger, or from the butyral of Chancel) and ammonia, butyrylamine, $\left.\begin{matrix} C^8 H^7 \\ H \\ H \end{matrix}\right\} N$; and by the action of the bromide of butyryle upon this base, dibutyryleamine (coniine), $\left.\begin{matrix} C^8 H^7 \\ C^8 H^7 \\ H \end{matrix}\right\} N$, for—

I. $C^8 H^7 Br, NH^3 = C^8 H^9 N + BrH.$
Brombutyryle. Butyrylamine.

II. $C^8 H^9 N + C^8 H^7 Br = C^{16} H^{15} N + BrH.$
Butyrylamine. Brombutyryle. Coniine.

Adopting the formula $C^{16} H^{15} N$ for coniine, this base becomes metameric with caprylnitryle, that is to say with the cyanogen æther of the radical of the alcohol of œnanthic acid, $C^{14} H^{15} + C^2 N$.—*Journ. für Prakt. Chem.*, Nov. 30, 1850.

ANALYTICAL CHEMISTRY.

Description of a new Method of determining the Amount of Oxygen in the Atmosphere. By Prof. J. Liebig.

The admirable methods with which MM. Regnault and Bunsen have enriched science are calculated for persons accustomed to manipulate with complex physical apparatus. They require a certain aptitude and skill, and an expense of time, which renders their employment exceedingly difficult or nearly impossible in innumerable cases in which it would be useful to know the amount of oxygen and carbonic acid present in the atmosphere. I have especially in view the physiologist desirous of obtaining the amount of oxygen and carbonic acid of the expired air in a series of analyses to be made daily for a number of days, or the technologist desirous of examining the air escaping from a furnace, or the physician wishing to know the composition of the atmosphere in a sick-chamber or the effect of ventilation. A method adapted for these purposes must not require any very complicated apparatus and no remarkable handiness; they must be quickly and easily performed, and possess a certain degree of accuracy. Now an alkaline solution of pyrogallic acid, the remarkable absorbent capacity for oxygen of which has long been known, combines all these conditions. When some solution of caustic potash is conveyed into a tube filled with mercury, and then a solution of pyrogallic acid, the liquids mix without any alteration; but if now a bubble of oxygen or of air be passed into the tube, the liquid immediately acquires a blackish-red or nearly black colour, and the oxygen is as rapidly absorbed as carbonic acid by caustic potash. The quantity of oxygen which is absorbed under these circumstances by 1 part by weight of pyrogallic acid is enormous. According to the experiments of Döbereiner, 1 grm. of pyrogallic acid in an ammoniacal solution absorbs 0·38 grm., or 260 cub. centim. of oxygen; this is more than the quantity absorbed by 1 part in weight of sodium on its conversion into oxide, which only amounts to 236 cub. centim. In one experiment, which was made with especial care, a solution of 1 grm. pyrogallic acid in caustic potash absorbed 189·8 cub. centim. oxygen. Since 1 grm. hydrate of potash (KO, Aq), in order to pass into neutral carbonate, absorbs at 32° F. 192 cub. centim. carbonic acid, the absorbent capacity of pyrogallic acid for oxygen, it will be seen,

is not less than that of potash for carbonic acid. The following results, which were obtained with atmospheric air, will give an idea of the accuracy which is obtained by means of this method:—

	Volume of air after introduction of the caustic potash.	Decrease in volume after introduction of pyrogallic acid.	Per cent. in volume of oxygen.
1.	221·5	46·5	20·99
2.	201·0	42·0	20·89
3.	193·0	40·6	21·03
4.	210·0	44·0	20·95
5.	204·5	42·5	20·77
6.	195·0	40·8	20·92
7.	200·0	41·8	20·90
8.	200·0	41·6	20·80
9.	200·0	41·5	20·75
10.	236·0	49·0	20·76
11.	258·0	54·0	20·93*

It will be seen that these determinations come very near to the best air analyses, and I have not the least doubt that they might be obtained quite as accurate if a cathetometer were used to read off the volumes, as is necessary in accurate measurements. We then, it is true, lose one of the chief advantages of this method, which consists in the circumstance, that it is possible to make in the course of an hour half a dozen analyses of sufficient accuracy for most cases. The reason of this extraordinary accuracy, notwithstanding all the errors attached to the method, is evidently owing to its great simplicity and the quickness with which the operation is completed; it is owing to this that the errors caused by a change of temperature and of atmospheric pressure vanish; and the influence of the errors peculiar to this method is apparently not greater than the influence of the sources of error in the most perfect which we possess. The following was the mode of proceeding in the above-mentioned analyses:—The air in which the amount of oxygen and carbonic acid was to be determined was measured in graduated tubes over mercury. The tubes would contain about 30 cub. centim., each cub.

* With the expired air of different persons I obtained the following results, some with gallic, others with pyrogallic acid:—

	Air.	Decrease in volume by solution of potash.	Decrease in volume by gallic or pyrogallic acid.	Volume of nitrogen.
1.	220·0	9·0	36·0	175·0
2.	221·5	9·0	36·0	175·5
3.	200·0	11·0	30·0	158·2
4.	194·0	10·0	29·0	155·0

Consequently the corresponding air in the experiments contains—

	I.	II.	III.	IV.
Carbonic acid	4·09	4·06	5·5	5·41
Oxygen	16·36	16·34	15·0	14·95
Nitrogen	79·55	79·23	79·1	79·90

These analyses have only been made to test the method, and have no value in a physiological point of view.

centim. divided into 5 parts; they were filled two-thirds with the air, the quantity read off, and now one-fortieth to one-thirtieth of its volume of solution of potash of 1·4 spec. grav. (1 part dry hydrate of potash to 2 parts water), introduced by means of the common pipette with curved point: by quickly moving up and down the tubes in the mercury, the solution of potash is spread over the whole inner surface of the tubes; and when no further decrease of space is perceptible, the decrease of volume is read off.

When the air has been previously dried by means of chloride of calcium, the decrease in volume accurately furnishes the amount of carbonic acid in the air; but if it were moist, the determination has an error attached to it, which is owing to the absorption of the aqueous vapour by the strong solution of potash.

After the carbonic acid has been determined, a solution of pyrogallic acid, containing 1 grm. of acid in 5–6 cub. centim. water, is introduced by means of a second pipette into the same tube, and amounting to about half the volume of the solution of potash. The same plan is adopted as in the determination of the carbonic acid, that is to say, the mixed liquids are well shaken over the inner surface of the tube, and when no further absorption is perceptible, the amount of nitrogen remaining is measured off.

By mixing the solution of pyrogallic acid with the potash, the latter is diluted, and an error arises from the diminution of its tension; but this appears to be so exceedingly small, that it is not determinable; at the same time, it may easily be avoided, if, after the absorption of the oxygen, a piece of solid hydrate of potash corresponding to the amount of water in the solution of pyrogallic acid is introduced, and its solution awaited.

Ordinary gallic acid may be employed instead of the pyrogallic acid with the same result; but its employment has this inconvenience, that the absorption of the oxygen requires a much longer time, at least one and a half to two hours, instead of as many minutes. Owing to the sparing solubility of gallic acid in water, it must be previously converted into gallate of potash, a cold saturated solution of which is employed. When this liquid is neutral or contains a very slight excess of acid, it does not experience any alteration in the air. Its property of absorbing oxygen only becomes active in the presence of an excess of alkali.

When the gallic acid has been mixed with the caustic potash in the tube, the liquid, on coming into contact with air containing oxygen, assumes a dark red colour; thin layers acquire almost a blood-red colour, which after a time passes into brown. By the production of this blood-red colour in the liquid, which moistens the sides of the tube on agitation, the progress of the absorption can be very distinctly traced; when this colouring is no longer exhibited, the operation is complete. With respect to the absorbent capacity of gallic acid for oxygen, it is known, from the experiments of Chevreul, that 1 grm. of gallic acid dissolved in strong potash absorbs 290 cub. centim., or nearly 0·417 grm. oxygen. In this respect it is in nowise inferior to pyrogallic acid.

The following experiments were made with gallic acid:—

	Volume of air after introduction of the potash.	Decrease of volume after introduction of the gallic acid.	Per cent. in volume of oxygen.
1.	269·5	55·5	20·59
2.	232·0	48·0	20·69
3.	217·0	45·5	20·97
4.	229·0	47·0	20·52
5.	191·0	40·8	21·35
6.	194·2	40·4	20·80
7.	192·5	40·0	20·78
8.	244·0	51·7	21·19

The differences in these determinations are far greater than with the employment of pyrogallic acid; but they are less attributable to the process than to the errors which are caused by the change of temperature and atmospheric pressure. In the first two, in the fourth and in the eighth analyses, the decrease in volume was measured off the following day; the numbers expressed the result, without any correction for the state of the barometer and of temperature.

Under certain circumstances tannic acid may be employed instead of gallic acid; but the mixture of tannic acid and potash absorbs oxygen still far more slowly than the gallic acid. Pyrogallic acid, which is easily obtained, is certainly the best absorbent. 150 analyses may be made with 1 oz. of pyrogallic acid, and its price certainly forms no impediment to its use.

Dr. Stenhouse has described a most excellent method for preparing pyrogallic acid. He obtained, by sublimation from the dry aqueous extract of the gall-nuts, precisely in the same manner as benzoic acid is prepared from benzoin resin, above 10 per cent. in sublimed acid of the weight of the extract. When those who are engaged in photography have become convinced that in many cases pyrogallic acid is preferable to gallic acid, the increased demand for this acid will render its preparation still more productive*.

The principal error in the above eudiometrical process, which is scarcely to be got rid of, is occasioned by the difficulty of accurately reading off and determining the volume of the air, and its decrease from the absorption of the carbonic acid and of the oxygen, owing to the adhesion of the liquids to the sides of the tubes. This error becomes smaller when the precaution is adopted of using nearly the same volume of air for each analysis; but though this method admits of perfectly trustworthy determinations in comparative analyses, it will not supersede the processes of MM. Dumas and Boussingault, or that of MM. Regnault and Reiset, or that of M. Bunsen for absolute determinations.

It need scarcely be mentioned, that the process I have described is only an application of the beautiful observations made by Chevreul and Döbereiner on gallic and pyrogallic acids, and that the merit of the discovery belongs to these illustrious individuals.—Liebig's *Annalen*, Jan. 1851, p. 107.

* By the dry distillation of so-called Chinese galls in small retorts capable of holding from 5 to 6 oz. in coarse fragments, a very concentrated solution of pyrogallic acid is obtained, which, evaporated on the water-bath, yields of brown crystalline pyrogallic acid nearly 15 per cent. of the weight of the galls.

On the Qualitative Determination of Tin, Antimony and Arsenic. *By* T. Fleitmann.

Although analytical chemistry possesses several methods of distinguishing between tin, antimony and arsenic, I am not acquainted with any process by which these three metals, when they occur together, can be recognised with the same ease and quickness as in the case of most other metals. At the same time, the frequent occurrence of these three metals together renders a quick mode of detecting them highly desirable. The following may be viewed as a small contribution towards this object.

With regard to the discrimination of tin and antimony, this is founded on the solubility of metallic tin in strong muriatic acid, and the insolubility of antimonial stains obtained according to Marsh's method in hypochlorite of soda.

When the muriatic solution of the two metals is treated with some metallic zinc, they are both precipitated, the antimony with disengagement of antimoniuretted hydrogen. When the precipitation is made in a small apparatus for the disengagement of hydrogen, the antimony is readily detected by the black stains insoluble in hypochlorite of soda, which it produces upon a piece of porcelain. When subsequently the precipitated metallic powder of tin and antimony is boiled with strong muriatic acid, only tin dissolves, forming protochloride, which, after subsequent dilution with water, is recognized by the brownish-black precipitate produced by sulphuretted hydrogen. Neither of these reactions are modified by the presence of arsenic.

The detection of arsenic when antimony is present is founded upon a remarkable difference which these two metals exhibit towards nascent hydrogen when the latter is disengaged from an alkaline liquid. When a strongly alkaline solution of antimony is heated with metallic zinc, antimony is precipitated simultaneously with a lively disengagement of pure hydrogen, which does not show the slightest reaction of antimoniuretted hydrogen. If, on the contrary, a substance containing arsenic acid is mixed with an excess of potash and some finely-divided zinc, the hydrogen given off on the application of heat is abundantly charged with arseniuretted hydrogen. The presence of this latter is ascertained most simply by holding a strip of paper dipped in nitrate of silver over the arseniferous mixture of potash and zinc ; with the slightest trace of arsenic the paper is coloured distinctly black.—Liebig's *Annalen*, Jan. 1851.

On some distinguishing Reactions of Arsenical and Antimonial Spots. *By* J. W. Slater*.

If a drop of bromine is placed on a saucer, and a capsule containing arsenical spots inverted over it, the spots take a very bright lemon-yellow tinge in a short time. Antimonial spots, under the same circumstances, are acted on much more rapidly (in about five seconds at a temperature of 52° F.), and assume an orange shade. Both become colourless if exposed to the air, and are again restored

* Communicated by the Author.

if treated with a strong solution of sulphuretted hydrogen. The secondary yellow of the arsenical spots, as observed by Lassaigne, disappears on the addition of ammonia, whilst that of antimonial spots remains untouched. A concentrated solution of iodate of potash turns arsenical spots of a cinnamon-red, and dissolves them almost immediately. On antimonial spots it has no visible action within three or four hours. Solutions of the hypochlorites (chlorides) of soda and lime and chlorine water dissolve arsenical spots instantaneously, leaving those of antimony. A concentrated solution of the chlorate of potash gradually acts upon arsenical spots, but not upon those of antimony. The nitroprusside of potassium, on the other hand, slowly dissolves antimony, producing no perceptible effect upon arsenic. The statement of Bischoff, that arsenical spots were soluble, antimonial insoluble, in a solution of the chloride of sodium, could not be verified, as, after repeated trials, it was found to leave both not perceptibly affected. The chloride of barium, the hydrochlorate and the sulphite of ammonia, afforded likewise no distinguishing action. The nitrate of ammonia dissolves arsenical more rapidly than antimonial stains. Of these reactions the most decisive are those of iodate of potash, hypochlorites of soda and lime, and fresh chlorine water.

Mech. Institution, Droylsden, Manchester, Jan. 16, 1851.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On Galvanic Soldering. By Dr. L. Elsner.

By the term "galvanic soldering" is understood the junction of two separate pieces of metal by means of metal precipitated by the galvanic current. This experiment of soldering by the wet way has been for some time past recommended in technical journals; while, on the other side, it has been asserted that a union of separate pieces of metals by this means could not be effected. In order to make this matter clear, I instituted the following experiments, the results of which speak favourably for galvanic soldering.

For carrying on the experiments, a "bladder apparatus" was made use of. As exciting fluids, there was used, on the one hand, a concentrated solution of sulphate of copper, with an excess of sulphuric acid, which occupied the exterior vessel; on the other, dilute sulphuric acid, which was contained in the inner portion, which is enclosed by a bladder. The block of zinc was plunged into the sulphuric acid, and a plate of copper, parallel with the bottom of the bladder, into the solution of sulphate of copper; both metals, of course, being connected by wires. On the plate of copper, which served as the negative electrode, was laid a ring of stout sheet copper, which was cut through at one point (the distance between the two cut ends might amount to from about the one-fourth to the one-sixth of a line). After several days, during which time the exciting fluids were repeatedly renewed, the space between the cut ends of

the ring was found completely filled with precipitated metallic copper. M. Knoblaut, the engraver, had the kindness to file a portion of the ring at the spot in which the ring had been cut; moreover, the magnifying glass showed the homogeneous filling up of the cut portion with coherent solid copper.

A second copper ring was divided into two parts; and the two halves, with their cut surfaces placed in apposition, were subjected to the same galvanic action. After several days, the two half rings were found completely united into one ring at their point of contact by solid precipitated copper. In this instance, also, filing a portion of the ring at one of the former points of contact, showed that this space was completely filled and solidly united by perfectly homogeneous precipitated copper. On examining this spot with the glass, the perfect homogeneous connexion of the previously-divided portions of the ring was very evident.

A third experiment was made in the following manner:—Two rings of stout sheet copper were so placed directly over each other as to form a cylinder, consisting of the two rings; moreover, the rings were surrounded with a strip of tinfoil, and this was painted over with a solution of wax in oil of turpentine, so that both rings were equally surrounded with a conducting mould. The rings, thus arranged, were laid on the copper plate of the "bladder apparatus," and plunged in the solution of sulphate of copper. After several days, the inner sides of the rings were covered with a deposit of copper, and the points of apposition between both rings filled up with galvanically-precipitated copper. The rings were no longer subjected to galvanic action, as but a moderately thick layer of copper was deposited on their inner sides: notwithstanding which, both rings were united into a completely solid cylinder. As a matter of course, the outer shell of tinfoil was removed before a trial was made of the solidity of the galvanic deposit. It is also to be remarked, that the rings, after being for some time in contact (during the galvanic action) with the plate of copper on which they reposed, were so firmly attached by the precipitated metallic copper as to require some application of force to separate them from it.

From the communication of the results of the foregoing experiments, it may be stated without any hesitation, that galvanic soldering is available to produce a solid connexion of separate portions of metal. Hence it follows, that the solid combination of separate moulded portions of metal into one entire form or figure, by means of galvanically-precipitated metal (usually copper), must be practicable. There is reason to believe that a galvanic soldering would be effected by means of concentrated solutions of the salts of gold and silver, as is the case with solutions of the salts of copper. M. Von Hackewitz informed me that he had remarked in his works on a large scale, and also in the galvanic precipitations of silver, that even in these galvanic union of distinct and separate portions had taken place.

In prosecuting the before-mentioned experiments, it was observed, that when the galvanic action was too strong, and also when the

current was too powerful, the negative copper electrodes, as well as the plate of copper and the copper rings resting on it, were covered with a dark brown coating (as is well known to be the case under similar circumstances in galvanic gilding). After many fruitless attempts to get rid of this brown coating, it was discovered that it could be easily and perfectly effected by immersing for some seconds, in a mixture of sulphuric and nitric acids, the articles thus coated. This brought out afresh the beautiful red colour of the galvanically-precipitated copper; and after the articles were thoroughly washed with water, and again subjected to galvanic action, a fresh precipitation of copper took place.

That galvanic soldering must have a practical application may, in few words, be deduced on theoretical grounds. The articles are electro-negative, while the zinc is positive; consequently they are negative at the opposite points of section, *i. e.* subject to the same electric action; therefore, during the electrolytic decomposition of the metallic salt (in the above instance sulphate of copper), the separating electro-positive particles of copper are deposited on both the opposite cut surfaces. Being once deposited on the immersed article, they form with it a homogeneous whole; and they now act negatively on the copper still remaining in the solution, and again metallic copper is precipitated on it. This process will and must continue until the space between the pieces of metal is filled with galvanically-precipitated copper, as is proved by experience; for the space between the opposite cut surfaces becomes smaller and smaller by the deposit on them of the precipitated copper; and when the deposited particles of metal finally come in contact, the former intervening space is completely filled with copper.

As regards the solidity (the degree of cohesion) of the galvanic soldering, it is the same as that of the galvanically-precipitated copper, or in general that of the precipitated metal; moreover, that the cohesion of the precipitated metal is and must be influenced in proportion to the vigour of the galvanic action is self-evident, and precisely the same phænomenon will take place in this case as has been witnessed in galvano-plastic operations.

In the foregoing experiments, the simple or single bladder (diaphragm) apparatus was made use of, although, as far as I know up to this time, any constant element has been employed; but since, by the application of the simple bladder apparatus, the same results have been obtained as by the application of the hydro-electric constant elements, it is a further confirmation of the practical applicability of the galvanic soldering.

M. Philipp states, that when a ring, open at one place, is to be galvanically gilt, no deposit takes place at the ends, but that it is thicker in proportion to its distance from its ends. I have repeated these experiments with bronze rings (of copper and brass), and found that the rings were all over completely and uniformly gilt and silvered, and consequently on the opposite ends of the cut portions, which, agreeably to the theory, could not be otherwise.—Newton's *Journal.*

THE CHEMICAL GAZETTE.

No. CC.—February 15, 1851.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Composition of the Walls of the Cells in Plants; with Observations on the Potato Disease. By Prof. MITSCHERLICH.

THE paper which is prepared in Sweden with pure water consists of pure cellulose; within the liber-cells of the flax a substance is often also left behind, which is coloured brown by iodine, and when subsequently moistened with sulphuric acid does not become blue; it exists in small quantity only, and is almost entirely removed by the mechanical process adopted in the conversion of linen into paper, in which the individual cells are torn and crushed, and by the chemical agency during bleaching; a dilute solution of soda removes the last traces of it, but at the same time slightly alters the composition of the cellulose. The liber-cell consists, as may be easily shown by boiling paper with muriatic acid, of separate longitudinal fibres lying in proximity to each other, primitive fibres; this structure, and the property possessed by cellulose of becoming moistened by water, are the cause that the liber-cell readily absorbs water and is very hygroscopic. Hence great care must be taken in drying and weighing it; accurate results may always be obtained by adopting the method described by the author in his Manual. The paper dried at 284° F. in a current of dry air yielded in 100 parts—

Carbon	43·99
Hydrogen	6·20
Oxygen	49·31
Ash	0·50

The paper, after having been boiled for a long time with solution of soda of 1·060 spec. grav., becoming at the same time somewhat coloured, yielded in 100 parts—

Carbon	45·70
Hydrogen	6·24
Oxygen	48·79
Ash	0·27

This ash consisted principally of carbonate of lime.

It follows from the first experiment that cellulose consists of 12 C, 10 H, 10 O, and not, as Mulder concludes from his experiments, of 24 C, 21 H, 21 O; the paper is slightly decomposed by the solution of soda, although the result of the second analysis is

also in favour of the same composition. If the action of the alkaline solution upon the cellulose be allowed to continue further, it becomes coloured blue by iodine; and when the solution is so concentrated that hydrogen begins to be developed, a residue is left, on the addition of water, possessing the form of the cellulose, and which is coloured dark blue, or almost black, by iodine; and water dissolves a combination of potash with cellulose, from which the latter is thrown down by an acid. Brown and black compounds, resembling ulmic and humic substances, are not formed during this reaction.

That the above composition is the correct one is also rendered probable by the fact, that by the action of dilute sulphuric acid the substances of the group to which cellulose belongs are either transformed into isomeric modifications, or take up water, but water is never separated from them. The complete conversion of cellulose by sulphuric acid into starch and dextrine without the formation of any perceptible accessory product, is the best criterion of its purity. That starch is really formed may be best shown by placing a long thin strip of pure filtering paper upon a plate of glass, moistening it, and then allowing a drop of sulphuric acid to fall upon the middle of it, and waiting until microscopic examination shows that the liber fibres are perfectly swollen up in some spots; for they swell up under these circumstances as much as starch does when acted upon by hot water; the expansion usually amounts to more than fourfold in one direction; it then forms a gelatinous pasty mass; if water be then allowed to flow upon the paper until the sulphuric acid is washed away, and it is then moistened with a solution of iodine in iodide of potassium, it may be seen distinctly that all those portions which are sufficiently swollen acquire the well-known beautiful blue colour; and when this colour has disappeared from exposure to the air, it may be reproduced by the addition of the solution of iodine. If the sulphuric acid be allowed to act upon the middle of the strip until the cellulose is dissolved, and it is then washed away, we find, from this portion of the paper to that which has remained undecomposed, all the modifications which are produced by the action of sulphuric acid upon cellulose up to dextrine.

Nitric acid of 1·20, when cold, exerts no action upon cellulose, and in the water-bath but very little.

The change which cellulose undergoes by the action of a peculiar ferment is of very remarkable interest and characteristic of the substance. This fermenting agent is obtained when half-putrid potatoes cut up into pieces are placed in water with portions of fresh potatoes, and allowed to stand in a not too cold place until the cells of the fresh portions begin to be easily separable; it is also formed, but more slowly, when fresh potatoes, cut up, are set aside covered with water. The liquid is filtered, and fresh potatoes cut in slices added to it; when these are decomposed, a portion of the liquid may be treated with water, and more slices of potato added, which soon become decomposed, and in this manner increase the activity of the liquid. Hence, just as in the fermentation of an infusion of

malt, the yeast, the fermentative fungus, becomes augmented, so does this ferment increase. It only acts upon the cellulose, which, without any other admixture, forms the walls of the cells of the potato which are filled with starch; first, the cells separate from each other, so that it furnishes us with a more convenient and perfect means of obtaining the cells with their contents separate from each other, and facilitating their examination; the walls of the cells are subsequently also dissolved, and the starch particles fall out; in this manner in twenty-four hours a slice of potato is rendered so soft to a depth of 2 lines, that this portion can be removed by a pair of forceps, the hard mass of the potato lying beneath the softened layer; so that this process takes place successively from the outside towards the interior; not by the whole of the potato being simultaneously permeated by the ferment to the innermost portion. No trace of a fungus can be found in the active liquid; it is however full of Vibrions, which may in this case be the effective agents. The author is in hopes of discovering the substance into which the cellulose is converted; hitherto he has not succeeded in obtaining it. Exactly the same process as that which we can produce spontaneously, occurs in the potato disease, which during late years has done so much mischief. In this also, the cellulose, and not the starch, is decomposed; and the liquid, which the author had kept for a long time in contact with one of the diseased potatoes, immediately produced the decomposition of a sound one. This decomposition is therefore not the disease itself, but merely the result of it. Its cause undoubtedly depends upon the dying, or the previous death, of the entire plant; and just as it is well known in the case of other plants, that they die when the apices of their roots are too strongly cooled, so may a sudden cold rain, following a long warm winter, produce a similar condition of the potato plant.

There is another solution of cellulose, which is also of peculiar interest in regard to vegetable physiology,—cellulose which has been deposited; and when the walls of the cells consist of it alone, the entire walls of the cells become dissolved and disappear. This may be most distinctly and beautifully traced during the germination and development of plants, when taking place at the expense of substances which have been deposited. Seeds of the cerealia are allowed to germinate in contact with water only, by causing the grains first to germinate between pieces of wet paper, and then to develope themselves in glasses filled with water; a glass plate, furnished with small holes, being placed upon the surface of the water, the roots are placed in these holes, the grain resting upon the plate. In this experiment, the alterations undergone by the starch itself may be observed; in three or four weeks it is seen that the point of the first leaf begins to turn yellow. This is a sign that all the starch is consumed; if the grain be examined, the interior is perfectly empty, not only the starch, but also the cellulose having disappeared; the plant continues to live for a certain time, the young leaves being nourished by the absorption of the constituents of the older ones; the plant however soon dies, because it cannot obtain

in this manner those constituents derived from the soil which are necessary to its nutrition; in the potato disease, the cause of the death of the plant may be the death of all the delicate points of the roots, when they are consequently unable to derive the requisites for the continuance of their existence and their development from the soil. In the parent potato plant, during the development of a new plant from it, absorption of the cell-wall does not take place; usually a considerable part of the cells is still full of starch, so that for the new plants to be developed so as to acquire their independence, a portion only of the parent potato is requisite. The absorption of the cellulose takes place also in pith; the walls of the young cells of the pith of the elder consist entirely of cellulose in the spring, whilst those of the previous year no longer contain any of it. Cork, which is, next to cellulose, the most important constituent of the cell-wall, is so difficult to obtain in a state of purity, that the author does not venture at present to express any opinion upon its composition; when obtained in a pure state, another name must be given to it. It sometimes forms a thin, shapeless, continuous coating of the entire plant; sometimes it constitutes the outermost cellular layer of the stem; very often it forms several cellular layers, as in the potato. In the latter it forms a row of cells, readily distinguishable both by their structure and chemical reactions from the subjacent cells containing starch; the number of superimposed layers is different in different varieties of the potato. This layer is easily separable from boiled potatoes, and from the cells consisting of cellulose which are filled with starch. This substance is very readily distinguishable from cellulose by its reactions with nitric and sulphuric acids. Concentrated sulphuric acid, which immediately dissolves cellulose, does not act upon this substance until the lapse of a very considerable time; thick cell-walls resist its action longer than thin ones; at last, especially on the application of heat, brown products are formed. Nitric acid of 1·2 spec. grav. oxidizes it, even below the boiling-point of water; the cells first swell, and the product is then soluble in potash; the cells soon separate from each other, and by the continued action of nitric acid a series of acids are formed, the final members of which are suberic and succinic acids. The first products are red, the colour becoming more intense when combined with alkalies; they are fusible at the boiling-point of nitric acid, and soluble in alcohol. The same products are obtained, but in different quantities, when cork, the peel of potatoes, or even the cuticle of *Aloe lingua*, which resists the action of sulphuric acid for several days, is boiled with nitric acid of 1·2 spec. grav. In the water-bath the corky matter is so readily oxidized by nitric acid, that when cells of cellulose are mixed with its cells, the latter remain unaltered, on filtering the residue and exhausting with alcohol as soon as nitrous vapours cease to be perceptible. We sometimes meet with thick-walled cells of cellulose, which exactly resemble those of the stone of stone-fruits, but which also occur frequently in the bark of many trees and in the cork-layer of the oak.

After deducting the cellulose, the ash and the substances soluble

in alcohol, the corky layer of potatoes was found to consist per cent. of—

Carbon	62·3
Hydrogen	7·15
Oxygen	27·57
Nitrogen	3·03

With nitric acid, 100 parts gave 6·2 parts of a fatty acid soluble in alcohol.

Cork from the cork-oak, carefully separated by excision from the brown matter running transversely across it, yielded per cent.—

Carbon	65·73
Hydrogen	8·33
Oxygen	24·54
Nitrogen	1·50

Another quantity of the same piece, treated in the same way with nitric acid, yielded 39·67 per cent. of a fatty acid and 2·55 per cent. of cellulose. Alcohol extracted from 100 parts of the same cork 1·15 part of a fatty matter difficultly soluble, and 5·4 of a fatty substance readily soluble in this menstruum. The cork was used for analysis without any previous treatment, and in a perfectly dried state. The composition given by Mulder for the cuticle of *Agave Americana* nearly agrees with the above, as does also that of cork given by Döpping.

Exuberant growth of cork-cells is common. In *Cornus alba*, and most trees, it is seen on the young branches; we either meet with a mere tumid state of the bark, or the exuberant growth increases to such an extent, that rupture of the uppermost layers of cells takes place; hence, as the exuberant growth proceeds to a greater extent in few plants only, lenticular glands are formed. In the cork-maple this exuberance is greatest on the lower branches, which are surrounded by moist air, so that a copious formation of cork occurs upon them; it does not however form a connected layer as in the cork-oak. Exactly the same exuberant growth occurs in the potato. The tuber is the end of an underground stem, which has become thickened; the stem is usually furnished with only a single layer of cork-cells; the tuber itself has five or six such layers, frequently still more. Both on the stem, and especially at the tuber, small swellings are perceptible, even while both are quite young. A transverse section of these shows that they are formed by an increase of the cork-cells; when coloured with iodine, they are not rendered blue by sulphuric acid; they are not altered by it, whilst the adjacent cells, which consist of cellulose, are immediately dissolved. On the further development of the tubers, the number of cells at these spots rapidly increases, and in much greater proportion than that of the other cells, so that the outermost become separated from each other. In the full-grown tubers, deep cavities or pits, originate in this manner; these are covered with cork-cells, but are not closely connected, so that the moisture of the soil is able to penetrate in an unchanged state to the more deeply situated starch-cells. A process of decomposition commences at these spots,

by which the agriculturist, on keeping them through the winter, frequently loses half his crop of potatoes.

The corky layer is difficultly permeated by water; it thus protects the plants, not only from liquid, which might penetrate from without, but it also prevents their drying. Potatoes, the surface of which is uninjured, may be kept for months without becoming the least flaccid, and losing scarcely anything in weight. The author has kept potatoes in a drying chamber at a temperature slightly above 86° F. for months. Uninjured potatoes lost about 3 per cent. in weight; the pitted ones almost twice as much. Potatoes which had been cut through the middle shrunk up in a few days, and when cut in slices, they were almost perfectly dried in the same time. Even below 212° F. the cork of the oak parts with all its water in a drying apparatus; and the small extent to which it transmits water and liquids is best shown by its common application to the closure of bottles filled with liquids.

A layer of corky substance, in fact, prevents the penetration of moisture. Conviction may readily be obtained by means of iodine and sulphuric acid, that the most delicate vegetable hairs are covered by a thin layer of corky substance (cuticle). Fresh cotton-wool imbibes water with difficulty. If the corky layer be removed by chlorine, or some other oxidizing agent, the wool may be moistened as readily with water as any other substance which consists only of cellulose.

Before treatment with chlorine, cotton-wool can hardly be impregnated with mordants; unbleached cloth becomes coloured in spots only, perhaps only between the fibres (hairs); whilst, as any one may readily convince himself by the examination of sections under the microscope, the cotton-wool fibre is coloured to the middle when it has been previously bleached.

The author considers it as not improbable, that cellulose and the corky substance, with the fatty matters covering them, are secreted by the same cell; and when the cellulose has been absorbed, the corky substance alone remains; moreover that the corky substance forms the outermost part of the cell-wall, and connects (cements) the cells with each other, just as the walls of the cork-cells are so thick, and so closely placed together, and so intimately connected with each other, that the wall belonging to each cell cannot be distinguished. This circumstance may also yield an explanation of the reason why the cells of wood, the stones of stone-fruits, &c. are so readily separated from each other, which can be so beautifully effected by ebullition with nitric acid, especially when a little chlorate of potash is added to it according to Schultze's direction.—*Ann. der Chem. und Pharm.*, lxxv. p. 305; *Reports of the Berlin Academy*, March 1850, p. 102.

✓ *Observations on the Sulphuret of Gold, and Determination of the Atomic Weight of Gold by a new Method. By* A. Levol.

Nearly all works on chemistry mention two sulphurets of gold, the protosulphuret, Au^2S, which is said to be produced by the ac-

tion of hydrosulphuric acid upon a boiling solution of sesquichloride of gold, and the sesquisulphuret, $Au^2 S^3$, which is formed by the action of the same substances in the cold; they however do not agree with regard to the characters of the two compounds.

The results which M. Levol has arrived at are very different. Having passed a current of hydrosulphuric acid into a boiling solution of chloride of gold, he obtained a brownish-yellow precipitate, which on examination proved to be pure gold; its weight represented exactly the amount of gold which the solution contained; and the estimation of the sulphuric acid formed in this reaction agreed precisely with the following theoretical formula, which expresses the decomposition:—

$$4Au^2 Cl^3 + 3HS + 9HO = 8Au + 12HCl + 3SO^3.$$

Thus, in the above conditions, the sesquichloride of gold is completely reduced by the hydrosulphuric acid, and no protosulphuret of gold is formed.

When sulphuretted hydrogen is passed into a solution of chloride of gold at the ordinary temperature, a homogeneous black precipitate is obtained, which pertinaciously retains water, and its weight only becomes constant by desiccation at 284° F. This sulphuret is pretty stable, not being altered when boiled in the liquid in which it was formed; and when heated it only begins to be decomposed above 392°. This sulphuret contains very nearly 14 per cent. of sulphur, which corresponds to the formula $Au^2 S^2$, or $Au^2 S + Au^2 S^3$. This composition, confirmed by the determination of the amount of sulphuric acid, which is formed at the same time as the sulphuret, shows that the reaction by which it is produced is expressed by the formula—

$$4Au^2 Cl^3 + 9HS + 3HO = 4Au^2 S^2 + 12HCl + SO^3.$$

It results therefore that if the two sulphurets, said to exist, can really be obtained, it is certainly not under the circumstances stated.

Berzelius determined the equivalent of gold by ascertaining the weight of mercury required to decompose the chloride of gold, and by the analysis of the aurochloride of potassium. The first method led to the number 1243, which was for a long time admitted by chemists; but the recent correction of the equivalent of mercury has reduced that number to 1227·45. The second method gave for result 1229·41. M. Levol has determined this equivalent afresh by a different method; it consists in converting a known weight of pure gold into chloride, decomposing this salt by a current of sulphurous acid, and weighing the sulphuric acid formed in the state of sulphate of baryta—

$$Au^2 Cl^3 + 3SO^2 + 3HO = 2Au + 3SO^3 + 3HCl.$$

M. Levol found that 1 grm. of pure gold furnished in this manner 1·782 sulphate of baryta; whence he deduces for the equivalent of gold the number 1227·01, which is almost identical with that calculated according to the new atomic weight for mercury.

Ann. de Chim. et de Phys., Nov. 1850.

On the Constitution of Codeine and its Products of Decomposition. By Thomas Anderson, M.D.

[Continued from p. 49.]

V. *Products of Decomposition of Codeine.*

III. *Action of Sulphuric Acid.*

Amorphous Codeine.—When codeine is dissolved in an excess of moderately-concentrated sulphuric acid, and the mixture digested on the sand-bath, the fluid gradually acquires a dark colour, and after some time gives a precipitate with carbonate of soda, which the salts of codeine are incapable of doing. The precipitate so obtained is codeine in a modified or amorphous condition, similar to that in which quinine is obtained by a similar treatment with excess of acid. By carefully regulating the temperature of the mixture of codeine and sulphuric acid, the amorphous codeine may be obtained in a state of purity; but it is neither so definite nor so stable a substance as quinoidine. After the action has been prolonged for some time, carbonate of soda is added to the fluid, and the gray precipitate obtained collected on a filter, washed with water, dissolved in alcohol, and precipitated from the solution by means of water. As thus obtained, it is a gray powder, with a more or less green shade, insoluble in water, readily soluble in alcohol, and precipitated by æther from the solution. It fuses at 212° into a black resinous mass. In acids it is readily soluble, with the formation of salts which are amorphous, and dry up by evaporation into brown resins. Analysis gave the following results:—

	I.	II.	
Carbon	71·92	72·53	72·24
Hydrogen	7·53	6·84	7·02
Nitrogen	..	..	6·68
Oxygen	..	..	16·06

These results correspond sufficiently closely with those of codeine to show that this substance is represented by the same formula. At the same time it is to be observed, that the action does not stop at the point at which amorphous codeine is formed; for the excess of carbon and deficiency of hydrogen in the second analysis (which occurred also in another analysis from a different preparation) appear to me to show that some further change had taken place. Indeed, by continuing the action of sulphuric acid, a deep green powder was obtained, which contained sulphur, and agreed in its general properties with the sulphomorphide described by Arppe, and the corresponding sulphonarcotide of Laurent and Gerhardt.

IV. *Action of Nitric Acid.*

Nitrocodeine.—When strong nitric acid is poured upon codeine, and heat applied, violent action takes place, nitrous fumes are abundantly evolved, and the solution acquires a red colour. If the fluid be evaporated on the water-bath, a yellow resinous acid is left, which

dissolves in ammonia and potash solutions, with a red colour*. If the nitric acid be employed in a sufficiently dilute state, a different result is obtained, and a nitrobase is formed, to which I give the name of nitrocodeine.

The preparation of this substance is a matter of some nicety, as by the continued action even of very dilute nitric acid it is rapidly destroyed. The operation succeeds best when the acid employed is of a specific gravity of 1·060. Acid of this density is heated in a flask, but not to ebullition, and finely-powdered codeine is added, and a moderate heat is sustained. In the course of a few minutes a small quantity of the fluid is poured out into a glass, and an excess of ammonia added; if no precipitate appears, the heat is kept up for a short time longer, and another quantity is then taken out and tested; and this is repeated until the precipitate, which makes its appearance when the acid is neutralized, ceases to increase. The fluid is then immediately saturated with ammonia, and stirred rapidly, when it becomes filled with a bulky precipitate of nitrocodeine. The action which takes place is extremely rapid, and the whole operation is complete in a few minutes; so that the experimenter requires to be carefully on the watch in order to hit the right moment for precipitating the fluid. No red fumes are evolved; if they are seen, it is a sure sign that the action has gone too far, and that part of the codeine has been converted into the resinous acid already mentioned. On this account it is better to stop the action before the whole of the codeine is decomposed, the quantity left being easily recovered from the solution; but even with the greatest possible care, the formation of a small quantity of the resinous acid cannot be avoided, and its presence is always indicated by the dark colour which the fluid acquires when saturated by ammonia.

On the addition of ammonia, the nitrocodeine falls in the form of minute silvery plates, with a very slight shade of yellow. It is purified by solution in hydrochloric acid, boiling with animal charcoal and a reprecipitation with ammonia, in order to separate colouring matter and any unchanged codeine which may have been precipitated along with the first crystals. The nitrocodeine is then crystallized by dissolving in dilute alcohol, or a mixture of alcohol and æther.

Nitrocodeine crystallized from alcohol is deposited in the form of slender silky needles of a pale fawn colour, which on drying mat together into a silky mass. From alcohol and æther it is obtained by spontaneous evaporation in small yellowish crystals, which under the microscope are seen to be four-sided prisms, terminated by dihedral summits. Nitrocodeine is sparingly soluble in boiling water, from which it is deposited in minute crystals on cooling. It dissolves abundantly in boiling alcohol, and but sparingly in æther. It is soluble in acids, with the formation of salts which are neutral to test-paper, and from which potash and ammonia precipitate the base as a crystalline powder. When heated carefully, it melts into a

* The constitution and properties of this substance will be detailed in a future communication.

yellow fluid, which concretes on cooling into a highly-crystalline mass. At a higher temperature, it suddenly decomposes without flame, leaving a bulky charcoal.

Its analysis yielded the following results, of which No. I. is from the base crystallized from the first precipitate by ammonia, before I had observed its tendency to carry down codeine with it, and which has therefore given a slight excess; the others are from the pure base. Crystallized nitrocodeine is anhydrous:—

	I.	II.	III.			
Carbon	63·10	62·83	62·49	36	216	62·79
Hydrogen	6·04	5·80	5·91	20	20	5·81
Nitrogen	..	..	..	2	28	8·11
Oxygen	..	..	..	10	80	23·29

These results correspond with the formula $C^{36}H^{20}(NO^4)NO^6$, derived from that of codeine by the substitution of NO^4, in place of an equivalent of hydrogen. It is confirmed by the analysis of its platinum salt, which was found to contain 17·88 per cent. of platinum, giving for the atomic weight of the base 345·8. The calculated atomic weight is 344.

Hydrochlorate of Nitrocodeine.—Nitrocodeine dissolves readily in hydrochloric acid, and the solution on evaporation leaves the hydrochlorate in the form of a resinous mass, which cannot be made to crystallize.

Sulphate of Nitrocodeine is obtained in a radiated group of short-pointed needles, which are neutral to test-paper, and very soluble in boiling water. It furnished 10·13 per cent. sulphuric acid.

The formula $C^{36}H^{20}(NO^4)NO^6\,HO\,SO^3$ requires 10·17.

Oxalate of Nitrocodeine crystallizes in beautiful yellow short prisms, readily soluble in water.

Platinochloride of Nitrocodeine.—This salt is precipitated from the solution of the hydrochlorate as a yellow powder, insoluble in water and alcohol. Its analysis gave the following results:—

Carbon	39·11	36 =	216	39·25
Hydrogen.....	4·09	21	21	3·81
Nitrogen	..	2	28	5·08
Oxygen.....	..	10	80	14·58
Chlorine	..	3	106·5	19·35
Platinum	17·88	1	98·7	17·93

8·670 grs. of the precipitated salt, dried by long exposure to the air, lost at 212° 0·569 grs. of water =6·56 per cent. 4 equivs. of water require 6·14 per cent. The formula of the salt is therefore $C^{36}H^{20}(NO^4)NO^6\,HCl+PtCl^2+4HO$.

When nitrocodeine dissolved in alcohol is treated with hydrosulphuret of ammonia in the water-bath, the solution gradually acquires a dark colour, and sulphur is deposited. When the action is complete, the filtered liquid gives with ammonia a brown amorphous precipitate, which, when dissolved in hydrochloric acid and boiled with animal charcoal, gives on precipitation a pale yellow base.

The substance so obtained is very different from nitrocodeine; it is extremely soluble in alcohol, and is deposited from it as an amorphous powder. Once only did I obtain definite crystals, which were brownish rhomboids, but in too small quantity to admit of examination. The amorphous base did not give satisfactory results; and as its preparation is extremely troublesome, I did not pursue its investigation further. Arguing from what we know of the other bases formed by the same process, its constitution ought to be $C^{36}H^{22}N^{2}O^{6}$, and it might be called azocodeine.

V. *Action of Bromine on Codeine.*

Bromocodeine.—In order to obtain this substance, bromine-water is added in small successive portions to finely-powdered codeine. The base is rapidly dissolved, and the solution loses its colour of bromine, but acquires a peculiar and characteristic red shade. After a certain quantity of bromine has been added, small crystals make their appearance, which are hydrobromate of bromocodeine; but these are only observed if the bromine-water has been thoroughly saturated, and are deposited in small quantity only, the remainder being retained in solution. When the whole of the codeine has been got into solution, ammonia is added, and bromocodeine is immediately thrown down as a silvery white powder. In this state it contains a small quantity of unchanged codeine. It is collected on a filter, washed several times with cold water, and redissolved in hydrochloric acid, from which it is reprecipitated by ammonia, and finally crystallized from boiling spirit. Bromocodeine is scarcely soluble in cold water; but by boiling, a somewhat larger quantity is taken up, and deposited again on cooling in minute prisms, terminated by dihedral summits. It is readily soluble in alcohol, particularly on boiling, and is best crystallized from spirit diluted with its bulk of water. The crystals in which it is deposited are always very small, but brilliantly white. It is scarcely soluble in æther. Exposed to heat, it melts into a colourless fluid, which is destroyed at a temperature slightly above its melting-point. It dissolves in cold sulphuric acid, and the solution when heated becomes dark-coloured. It is attacked by nitric acid, but much less rapidly than codeine itself.

Considerable difficulty was experienced in getting it absolutely free from codeine; and the first of the following analyses has given an excess in the carbon:—

	I.	II.			
Carbon	57·67	57·21	36 =	216	57·14
Hydrogen	5·44	5·44	20	20	5·29
Bromine	..	21·50	1	80	21·16
Nitrogen	..	..	1	14	3·70
Oxygen	..	..	6	48	12·71

The formula is therefore $C^{36}H^{20}BrNO^{6}$. Bromocodeine is capable of uniting with water in two different proportions, as appears by the determination of the loss by drying:—

11·784 crystallized bromocodeine lost at 212°			0·273 = 2·32 per cent.	
9·308	...	...	0·623 = 6·69	...
7·707	...	..	0·512 = 6·64	...

The first of these results corresponds exactly to 1 equiv. of water, the calculated result for which gives 2·32 per cent. The other two give 3 equivs., for which the calculation is 6·66. I am unable now to recollect how the bromocodeine used in the first experiment was obtained, but my impression is that it was prepared in exactly the same manner as the rest.

Hydrochlorate of Bromocodeine is obtained in radiated needles, closely resembling those of hydrochlorate of codeine.

Hydrobromate of Bromocodeine.—The crystals which have been mentioned as making their appearance during the preparation of bromocodeine, are this salt. It is sparingly soluble in cold water, readily soluble in boiling water, and is deposited from the solution in small prismatic crystals. It contains 2 equivs. of water, which are not expelled at 212° :—

Carbon	45·18	36 =	216	45·28
Hydrogen.....	5·25	23	23	4·84
Bromine	..	2	160	33·54
Nitrogen	..	1	14	2·93
Oxygen.....	..	8	64	13·41

The formula of the salt is therefore $C^{36}\,H^{20}\,BrNO^6\,HBr+2HO$.

Platinochloride of Bromocodeine is precipitated as a pale yellow powder, insoluble in water and alcohol. It furnished, dried at 212°, 16·98 per cent. of platinum; the formula $C^{36}\,H^{20}\,BrNO^6,HCl\,Pt\,Cl^2$ requires 16·89.

Tribromocodeine.—By continuing the addition of bromine-water beyond the point at which bromocodeine is formed, a further action takes place, and a bright yellow precipitate makes its appearance, which at first redissolves in the fluid, but after a time becomes permanent, and goes on gradually increasing until a very large quantity of bromine has been employed, when at length a point is reached at which no further precipitate is produced. If the solution be left till next day, however, bromine again causes a precipitate; and if it be added as long as anything falls, and the solution be again left standing, another precipitate is produced identical in all respects with that before obtained; and this may be repeated day after day for a very considerable time. The yellow precipitate so obtained is the hydrobromate of tribromocodeine. It is collected on a filter, and washed with water, in which it is very sparingly soluble. In order to obtain the base, this substance is dissolved in dilute hydrochloric acid, and ammonia added, when the tribromocodeine is immediately precipitated as a flocky powder, which is washed with water, and purified by solution in alcohol and precipitation with water.

Tribromocodeine is thus obtained as a bulky white precipitate, perfectly amorphous, and when dry more or less gray in its colour. It is insoluble in water and æther, but readily soluble in alcohol. It

is sparingly soluble in hydrochloric acid in the cold, but much more so by boiling. In this process, however, it appears to undergo a partial decomposition, as a small quantity is always left insoluble. Heated on platinum foil, it becomes brown, and is entirely decomposed at its melting-point, leaving a coal difficult of incineration.

The tribromocodeine employed for analysis was purified by a second solution in alcohol, and precipitation by æther. It gave the following results:—

Carbon	39·69	36 =	216	40·27
Hydrogen.....	3·66	18	18	3·35
Bromine	44·68	3	240	44·72
Nitrogen	..	1	14	2·61
Oxygen.....	..	6	48	9·00

These results agree sufficiently well with the formula $C^{36}H^{18}Br^{3}NO^{6}$, produced by the substitution of 3 equivs. of bromine; and this formula has been confirmed by the analysis of its platinum salt, which will be given below.

In such cases as have been hitherto examined, the substitution of 3 equivs. of bromine in a base has entirely destroyed its basic properties, but tribromocodeine is still a base, though an extremely feeble one. Its salts are all sparingly soluble in water and amorphous; and as there is no possibility of ascertaining their purity, I have not pursued their investigation to any extent.

Hydrochlorate of Tribromocodeine.—It is obtained by dissolving the base in hot dilute hydrochloric acid, and is deposited on cooling as an amorphous powder.

Hydrobromate of Tribromocodeine.—This is the substance deposited during the preparation of tribromocodeine. It is a bright yellow powder, perfectly amorphous, and very sparingly soluble in cold water. On boiling, however, a larger quantity is taken up, and deposited unchanged on cooling

Its analysis gave the following results:—

	I.	II.			
Carbon.....	32·24	32·18	72 =	432	32·84
Hydrogen	2·83	2·86	39	39	2·96
Bromine	..	55·03	9	720	54·75
Nitrogen	..	..	2	28	2·12
Oxygen	..	..	12	96	7·33

These results approach most nearly to the formula $2(C^{36}H^{18}Br^{3}NO^{6}) + 3HBr$. They present however a certain deficiency both in the carbon and hydrogen, and an excess in the bromine; but no other formula can be found at all approximating to the experimental numbers, and the recurrence of the results, in portions prepared at different times, leaves no doubt that this is their real constitution; and in all probability the error may be due to the salt retaining a small excess of hydrobromic acid. The constitution is therefore remarkable, and I am not aware of any similar salt having been before observed.

Platinochloride of Tribromocodeine.—Bichloride of platinum

throws down from solution of tribromocodeine, in hydrochloric acid, this salt in the form of a brownish-yellow powder, soluble in water and alcohol.

Dried at 212°, it furnished 13·07 per cent. platinum; the formula $C^{36}H^{18}Br^3NO^6HClPtCl^2$ requires 13·29.

I have reason to believe that the action of bromine upon codeine does not terminate with the production of the base now described; but its further action did not appear to afford any products of sufficient interest to induce me to prosecute the investigation in this direction. There must also no doubt exist a *dibromocodeine*, $C^{36}H^{19}Br^2NO^6$, but I did not meet with it in the course of my experiments, and have not made any special attempts to obtain it.

[To be continued.]

ANALYTICAL CHEMISTRY.

On the Use of Hydrogen in the Analysis of Minerals. *By* L. E. Rivot.

The reducing action of dry hydrogen, at a more or less elevated temperature, upon several metallic oxides, may be employed with great advantage in separating these oxides from other fixed bases on which this gas has no effect at any temperature. I have been able to separate very accurately, by means of hydrogen, the oxide of iron from the earths alumina, glucina, zirconia; the oxide of iron from the oxide of chrome, and the oxide of tin from silica. I shall first describe the mode of separation and the results I have obtained, and then give an account of the mode of analysis I have adopted for chrome-iron and tin-stone.

Separation of Peroxide of Iron from Alumina.—The mode of separation described in the different works on analytical chemistry consists in treating the weighed mixture of the two oxides with potash, either by the dry way in the silver crucible, or by the humid way after solution in an acid, separating the oxide of iron, and well washing it with boiling water. This process is somewhat long, and frequently not very accurate when the potash employed is not perfectly pure. As the separation of these two oxides occurs very frequently in the analyses of minerals and other products, I endeavoured to discover a quicker and more accurate method, and have obtained most excellent results by reducing with dry hydrogen at a bright red the weighed mixture of oxide of iron and alumina precipitated by ammonia from an acid solution, letting them cool in the hydrogen, and then treating the mixture of alumina and metallic iron with cold very weak nitric acid; the iron dissolves very readily, whilst the calcined alumina is not attacked.

A few details will suffice to render the mode of proceeding intelligible. The oxide of iron and alumina are precipitated together by ammonia; the precipitate is dried, separated from the filter, the

filter burnt, and the ash united to the two hydrates, and the whole calcined in a platinum crucible at a red heat. The mixture of the two oxides is reduced to powder and accurately weighed; then placed in a counterpoised porcelain tray in a porcelain tube, arranged horizontally in a reverberatory furnace. A drawn-out tube is adapted to one of its extremities; whilst by the other, a slow current of hydrogen, dried over chloride of calcium and sulphuric acid, is introduced.

When the air of the apparatus has been completely expelled, the porcelain tube is gradually raised to a red heat, and this temperature maintained as long as water is seen to be deposited on the sides of the glass tube at the end of the apparatus. In all my experiments I never required more than one hour of firing to complete the reduction. The tube is then let cool, continuing the current of hydrogen; when perfectly cold, the tray is drawn out and weighed; the loss indicates the oxygen of the peroxide of iron, from which the proportion of the latter in the mixture can be calculated. However, it is not advisable to stop at this determination; when the quantity of alumina present is large, and when the gas has not been passed over very slowly, a little alumina may have been carried away by the hydrogen, and consequently the loss in weight would show too high a proportion of peroxide of iron.

The mixture of metallic iron and alumina is digested for about twenty-four hours in the cold with very weak nitric acid. The ordinary pure acid should be diluted at least with 30 times its volume of water or more, or the mixture placed in some pure water, and small quantities of nitric acid added at different intervals, so as to maintain a very slow effervescence of hydrogen; in this way the iron is sure to be completely dissolved, without the alumina being attacked. The solution of the iron is complete when the alumina has acquired a nearly white colour. The alumina is separated by filtration; the nitric solution heated to peroxidize the iron, which is then precipitated by ammonia. In this manner the two oxides may be weighed separately.

When the amount of alumina is very small, a very accurate result is obtained, from the mere loss in weight of the mixture in hydrogen, considered as representing the oxygen of the peroxide of iron.

The following mixtures, accurately weighed, were submitted to experiment:—

	I.	II.	
Alumina	0·500	0·152	0·053 grm.
Peroxide of iron	0·500	0·427	0·526

I obtained the following numbers:—

	I.	II.	III.
Loss of weight in hydrogen	0·156	0·132	0·1616

corresponding to—

Peroxide of iron	0·510	0·431	0·527

Then weighing the oxide of iron and alumina, separated by weak nitric acid, I found—

	I.	II.	III.
Alumina	0·492	0·148	0·052
Peroxide of iron	0·498	0·428	0·524

It is evident that the separation of the two oxides by the above process is very accurate; that the two oxides can be accurately estimated by weighing directly the peroxide of iron, and calculating the alumina by the difference; and lastly, that the loss of weight in hydrogen leads to a somewhat too high amount of peroxide of iron when the proportion of alumina is large, from some being carried away by the current of gas; and, on the contrary, the result is very accurate when the quantity of alumina is small.

I should observe, that if the hydrogen is passed over a mechanical mixture of alumina and oxide of iron instead of the two oxides precipitated by ammonia, the alumina is far more easily carried away by the current.

To calculate the amount of peroxide of iron from the loss of weight in hydrogen, I adopted 339 as the equivalent of iron, having obtained in two experiments, made with the greatest care, by the reduction in hydrogen of 1 grm. of very pure peroxide of iron—

	I.	II.
Metallic iron	0·6931	0·6935 grm.

and the mean of these two very accordant numbers leads almost directly to the number 339.

Separation of Oxide of Iron from Zirconia.—The separation of these two bases by the reducing action of hydrogen on peroxide of iron is made with the same ease and the same accuracy as that of the oxide of iron and alumina. The result obtained by weighing the zirconia is more exact, because this earth being heavier than alumina is not perceptibly carried away by the current of gas. A stronger acid may also be employed, as the calcined zirconia does not dissolve in acids.

A mixture of 0·66 peroxide of iron and 0·377 zirconia lost in hydrogen 0·205, corresponding to 0·667 peroxide of iron. On subsequently weighing the zirconia and oxide of iron, I obtained 0·375 zirconia and 0·668 peroxide.

These numbers prove that the separation of the two oxides by the proposed method is accurate, and that the composition of the mixture may be deduced from the loss of weight, resulting from the action of the hydrogen, considered as oxygen of the peroxide of iron. This mode of separation is quicker and more accurate than any of those hitherto proposed.

Glucina and Oxide of Iron.—Like alumina, the glucina may be carried away by the current of gas when its quantity is considerable, in which case the composition of the mixture must not be determined merely by the loss of weight resulting from the action of the hydrogen. The metallic iron should be dissolved in exceedingly weak cold nitric acid.

A mixture of 0·815 peroxide of iron and 0·399 glucina lost in hydrogen 0·249, corresponding to 0·812 peroxide of iron. On subsequently treating the mixture of metallic iron and glucina with

weak nitric acid, I found 0·816 peroxide of iron and 0·397 glucina. This method therefore answers exceedingly well for oxide of iron and glucina.

I have not made any experiments on the separation of the oxide of iron from yttria and thorina.

The reducing action of hydrogen on the oxides of cobalt and nickel likewise admits of useful application for the separation of these oxides from alumina.

When, in an acid solution containing cobalt and nickel with alumina, the latter is thrown down by ammonia, the precipitate retains a certain amount of cobalt and nickel. By calcining the precipitate, treating it with dry hydrogen, and then with very dilute cold nitric acid, the alumina is obtained quite free from cobalt and nickel.

Oxide of Tin and Silica.—The mixture of oxide of tin and silica, after having been strongly calcined and weighed, is placed in a counterpoised porcelain tray in a porcelain tube. The current of hydrogen should be very slow, in order that no silica be carried away with the gas, and the temperature should not go beyond a dark red. The reduction of the oxide of tin is very rapid; after cooling in hydrogen, the mixture of metallic tin and silica forms a gray powder containing no metallic globules, unless too high a temperature has been employed or the oxide of tin was nearly pure. It is weighed; the loss in weight furnishes the amount of oxygen of the oxide of tin, and enables us to calculate approximatively the composition of the mixture; however, as a small quantity of the silica may have been carried away by the gas, it is advisable to dissolve the tin in aqua regia, to weigh the undissolved silica; and, in case its weight does not accurately correspond to the quantity of silica calculated from the loss experienced by the mixture in hydrogen, to estimate the amount of tin in the aqua regia. The following process I found to succeed best. I saturate the acids with ammonia, add sufficient hydrosulphate of ammonia to dissolve the tin entirely, and then decompose the sulphosalt of tin by hydrochloric acid, which gives the metal in the state of sulphuret; this, after being well washed, is carefully roasted, and converted into oxide of tin.

The following mixtures were submitted to experiment:—

	I.	II.
Oxide of tin	0·310	0·500
Silica	0·644	0·500
The loss in weight by hydrogen was	0·069	0·106

Calculating the oxide of tin from these numbers, the following should have been the composition of the mixtures:—

Oxide of tin	0·324	0·509
Silica	0·630	0·491

A considerable error, an excess in the quantities of the oxide of tin, is apparent. On treating with aqua regia, and determining the amount of tin by the method above indicated, I obtained—

	I.	II.
Insoluble silica	0·636	0·496
Oxide of tin	0·307	0·497

These numbers show that the error committed by regarding the loss in weight as oxygen of the oxide of tin, was owing to a small quantity of silica being carried away by the current of gas. When the quantity of silica is at all considerable, the amount of tin should always be determined, and the silica calculated from the difference.

Tin Ores.—The ores of the oxide of tin may be very rapidly analysed by means of dry hydrogen. When the mineral, reduced to a fine powder, is gradually heated to redness in a current of dry hydrogen, the oxides of iron and tin are completely reduced. The time requisite for the reduction is about an hour and a half for 1 to 2 grms. of the ore. It is allowed to cool in the hydrogen, then weighed, when the loss in weight gives the oxygen combined with the iron and the tin. By treating the substance with aqua regia, the iron and tin are dissolved; the gangue remains unattacked, and may be analysed in the usual way. Ammonia is added to the solution of tin and iron to saturate the acids, and a sufficiently large excess of sulphuret of ammonium to dissolve the sulphuret of tin; it is then allowed to digest for about twelve hours and filtered; the sulphuret of iron, after being well washed with water charged with hydrosulphate of ammonia, is converted into peroxide of iron; the sulphuret of tin in solution in the hydrosulphate of ammonia is precipitated by acetic acid, and converted by roasting into oxide of tin.

The weight of the peroxide of iron and of the binoxide of tin indicates the weight of the iron and of the metallic tin, whilst the loss in weight of the mineral in hydrogen shows the amount of oxygen combined with the two metals, and enables us to determine their state of oxidation. In the analysis of the tin ore of Piriac, I obtained the following numbers. This ore contains the oxide of tin in minute grains, a little protoxide of iron, some garnets and quartz:—

Weight of the ore reduced by the hydrogen..	1·1795
Loss by the hydrogen	0·1235
Weight of the insoluble gangue	0·5650
Iron dissolved in the aqua regia	0·1310
Tin dissolved in aqua regia.....	0·3624

These numbers give the following composition for the tin ore:—

Iron	0·111
Tin.....	0·3081
Oxygen.....	0·1047
Gangue.....	0·4790

I will observe, that the iron, tin and oxygen are nearly in the relation of—

4 equivs. of iron.
5 equivs. of tin.
12 equivs. of oxygen.

I shall not attempt to deduce a hypothesis from these numbers for the chemical formula of native oxide of tin. I hope soon to analyse several well-crystallized specimens, and to be able to determine the state of combination of the iron and tin with the oxygen. I have

given the preceding analysis merely to show the quickness with which the amount of iron and tin may be ascertained, by treating the finely-pulverized ore with hydrogen.

Oxide of Iron and Oxide of Chrome.—The process usually employed for the separation of the oxide of iron from the oxide of chrome is as follows:—Sufficient tartaric acid is added to the hydrochloric solution of the two oxides, that, on saturating the acids with ammonia, no precipitate is formed; the iron is then thrown down as sulphuret by the hydrosulphate of ammonia, and the chrome remains in solution. To determine the amount of chromium, the tartaric solution must be evaporated to dryness, then the tartaric acid destroyed by heat, and the oxide of chrome estimated as sesquioxide, Cr^2O^3.

This process is tedious, and the separation is not very accurate. The following is, in my opinion, quicker and more exact. It is founded on the circumstance, that hydrogen readily reduces oxide of iron at a red heat, but exerts no action upon the oxide of chrome.

The mixture of the two oxides precipitated by ammonia, weighed after calcination, is treated as above described for the mixture of alumina and oxide of iron; after cooling in hydrogen, the matter consists of metallic iron and oxide of chrome; the loss in weight is entirely due to the oxygen combined with the iron, from which the amount of this oxide may be calculated very accurately, and consequently the composition of the mixture. To verify this, the substance may be treated with cold weak nitric acid, in which the iron alone dissolves; the oxide of chrome is weighed, the peroxide of iron precipitated by ammonia from its nitric solution. These determinations are remarkably accurate. I submitted to experiment—

	I.	II.
Oxide of chrome	0·30	0·761
Oxide of iron	0·70	0·749
The losses in hydrogen were	0·213	0·230

They correspond to—

Peroxide of iron.....	0·705	0·7498

Then, treated with weak nitric acid, weighing the undissolved oxide of chrome, and precipitating the oxide of iron by ammonia, I obtained—

Oxide of chrome	0·30	0·761
Oxide of iron	0·704	0·750

Analysis of Chrome-Iron Ore.—This ore may be analysed with the greatest accuracy by the following process:—The finely-powdered mineral is placed in a porcelain tray, in a porcelain tube, placed horizontally in a reverberatory furnace, and submitted for four hours to a current of dry hydrogen at a bright red heat; the loss in weight is the oxygen combined with the iron; the substance treated by hydrogen is digested for twenty-four hours with weak nitric acid at a gentle heat. This acid dissolves the metallic iron and a trace of lime, but is without action on the oxide of chrome, silica and alumina.

The iron is precipitated by ammonia from its nitric solution. The undissolved portion is fused in a silver crucible with a mixture of 1 part nitre, 3 parts carbonate of soda and 3 parts caustic potash, and the mixture kept for one hour well fused at an incipient red heat. After cooling, it is dissolved in hot water; the liquid has a yellow colour. It is rendered acid with hydrochloric acid, and evaporated to dryness with alcohol, redissolved by hydrochloric acid, when the silica remains undissolved; the acid liquid contains the chlorides of chromium, aluminium and calcium. After filtration, to separate the silica, it is precipitated by ammonia; the precipitate contains alumina, sesquioxide of chromium and a little lime; it is brought upon a filter, dried, and calcined with the ordinary precautions, but taking care to raise the temperature to a bright red towards the end of the operation. To separate the lime, the strongly-calcined precipitate is treated with very weak cold acetic acid; the acetic solution is then united to the ammoniacal solution, the lime precipitated by oxalate of ammonia, and the liquid tested for magnesia.

The oxide of chrome and alumina are weighed, then calcined, the mixture treated with hydrochloric acid, which dissolves only the alumina, the undissolved oxide of chrome is weighed, and the alumina precipitated by ammonia. In case the alumina should be accompanied by a trace of oxide of chrome dissolved by the hydrochloric acid, it will be requisite to separate by means of potash.

I have only as yet been able to analyse one specimen of chrome-iron from Baltimore. The analysis gave the following numbers:—

	grm.
Weight of ore	1·581
Loss in weight by hydrogen	0·144
Peroxide of iron	0·475
Silica or titanic acid	0·035
Sesquioxide of chrome	1·002
Alumina	0·030
Lime	0·032

This mineral does not contain magnesia. The above numbers lead to the following composition of the ore:—

Peroxide of iron	0·3004
Alumina	0·0196
Lime	0·0202
Silica, titanic acid?	0·0221
Sesquioxide of chrome	0·6337

I will only make one remark on this composition. The oxygen of the peroxide of iron and of the alumina is very nearly half the oxygen of the oxide of chrome. Several minerals can be readily analysed by means of dry hydrogen. I hope soon to be able to complete the preceding observations, and to determine with some certainty the chemical composition of some substances which are attacked with difficulty by acids.—*Ann. de Chim.*, October 1850.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Chemical Researches on Gold. *By* E. Fremy.

Of all the metals that are most easily obtained in a pure state, gold is that which has been least investigated by chemists; the series of oxides of this metal is evidently incomplete, and the compounds which the oxides of gold are capable of forming with acids and alkalies are scarcely known. Nevertheless the chemical investigation of gold presents great interest. It is known that this metal, like arsenic, boron and silicon, has a special tendency to form acids by uniting with oxygen.

Before submitting to a fresh examination the principal compounds of gold, such as the chlorides, the purple of Cassius, fulminating gold, &c., I thought it was important previously to examine the combinations of the oxides of gold with the alkalies, which are now so extensively employed in gilding by the humid way.

The protoxide of gold, Au^2O, is decomposed, as is well known, when submitted to the action of alkalies, and is immediately converted into metallic gold and alkaline aurate. This oxide behaves like protoxide of tin, which under the influence of an excess of potash resolves itself into tin and stannic acid; it is consequently impossible to obtain combinations of the alkalies and of the protoxide of gold. The aurates, on the contrary, are easily formed. I have prepared them, and determined their composition.

I prepare auric acid by boiling the perchloride of gold with an excess of potash; when the liquid has become partly decolorized, I precipitate the auric acid by sulphuric acid; and in order to purify it, I dissolve it in concentrated nitric acid, precipitate the solution by water, and wash the auric acid until the liquid contains no nitric acid.

The auric acid thus obtained is insoluble in the oxyacids, and even in hydrofluoric acid, but it dissolves in hydrochloric and hydrobromic acids. It combines directly with potash and soda, and the solutions evaporated *in vacuo* deposit the aurates of potash and soda in crystals.

The aurate of potash, which I have especially studied, crystallizes in small silky tufts; it is very soluble in water. The solution has a yellow colour and an alkaline reaction. Below red heat the salt is decomposed into metallic gold and peroxide of potassium, with disengagement of oxygen. The analysis of the aurate of potash enabled me to determine the equivalent of auric acid and the general con-

stitution of the aurates. From my analyses it results that the aurate of potash has the formula $KO, Au^2 O^3, 6HO$. In the neutral aurates, the relation of the oxygen of the acid to the oxygen of the base is therefore as 3 : 1.

From the aurate of potash all the other metallic aurates which are insoluble may be prepared by double decomposition; these aurates sometimes dissolve in an excess of the precipitant; thus, for instance, the aurate of lime is very soluble in chloride of calcium.

The aurate of potash may be used as a bath for electro-gilding, but it cannot be used for gilding by immersion. In gilding by immersion by the process of Messrs. Elkington and Ruoltz, it is therefore probable that the compound of gold, which is formed by the reaction of alkaline bicarbonate upon the chloride of gold, is not aurate of potash.

The reaction of the aurate of potash upon the sulphite of potash is exceedingly interesting. When the sulphite of potash is poured into the aurate of potash, a yellow salt, crystallizing in long satiny needles, is immediately precipitated. I have given to this salt the name of aurosulphite of potash; its composition should be represented by the formula $Au^2 O^3, (SO^2)^3 + 5(KO, SO^2) + 5HO$. According to this, the salt would be viewed as resulting from the combination of sulphite of potash and neutral sulphite of the peroxide of gold; but all the reactions of this singular compound go to prove that the gold, oxygen and sulphur are not arranged in accordance with the preceding formula. It is difficult, in fact, to admit that auric acid, which does not enter into combination with the oxyacids, and which itself behaves like a true acid, should unite precisely with sulphurous acid, which so readily reduces it. Moreover, in this new salt, the principal reactions of auric acid are completely masked. It is better to represent the aurosulphite of potash by the formula $KO, Au^2 O^3 + 4[KO, (SO^2)^2], 5HO$, which shows that the salt is produced by the combination of 1 equiv. aurate of potash with 4 equivs. of bisulphite of potash. Taking into consideration the properties, production and composition of the aurosulphite of potash, I am inclined to consider this salt as resulting from the combination of the potash with a ternary acid formed of gold, sulphur and oxygen, and to class it consequently with those compounds which I obtained by mixing sulphites with nitrites, and which I have described by the name of *sulphonitrites**; the gold would replace the nitrogen which exists in the latter salts.

The aurosulphite of potash can only be preserved in the dry state or in alkaline liquids; as soon as it is placed in pure water, it gives off sulphurous acid, and soon deposits metallic gold; acids decompose it instantly. Under the influence of heat, solutions of the aurosulphite of potash give an exceedingly brilliant and adherent deposit of gold. It will acquire importance when I shall have shown that other metallic salts can, like the aurate of potash, combine with the sulphites to form compounds possessing a certain analogy with the sulphonitrites.—*Comptes Rendus*, xxxi. p. 893.

* Chem. Gaz., vol. ii. p. 507.

On the Constitution of Codeine and its Products of Decomposition. By Thomas Anderson, M.D.

[Concluded from p. 74.]

VI. *Action of Chlorine upon Codeine.*

We might anticipate that the action of chlorine upon codeine would be exactly similar to that of bromine; but this is not the case, as in place of a simple and definite action, complex products are immediately obtained. When a current of chlorine is passed through an aqueous solution of codeine, the fluid immediately acquires a brown colour, which soon becomes very deep, and eventually almost black. From this solution ammonia throws down an amorphous resinous base. With chlorine-water the solution also becomes rapidly brown, and a similar precipitate is obtained. As there was no method of determining in either of these cases when the action was complete, I did not attempt to examine the product. I succeeded better, however, by the action of chlorate of potash, and obtained a base corresponding to bromocodeine.

Chlorocodeine.—For the preparation of chlorocodeine a sufficient quantity of codeine is dissolved in an excess of dilute hydrochloric acid at the temperature of about 150° or 160°. Finely-powdered chlorate of potash is then added, and the solution agitated. In the course of a few minutes a small quantity of the fluid is tested with ammonia, in order to see whether a precipitate is formed; and the action is allowed to go on until this is obtained, and the chlorocodeine is then precipitated by a slight excess of ammonia. The successful performance of this experiment requires exactly the same precautions as the preparation of nitrocodeine; and unless the action is stopped at the right moment, further products of decomposition are obtained. The reaction which takes place is represented by this equation:—

$$3(C^{36}\,H^{21}\,NO^{6}\,HCl)+3HCl+KO\,ClO^{5}=KCl+6HO+3(C^{36}\,H^{20}\,Cl\,NO^{6}\,HCl).$$

The chlorocodeine is precipitated in the form of a silvery crystalline powder, closely resembling bromocodeine; it has generally a yellowish colour, and the fluid from which it has deposited is coloured dark red by the presence of a small quantity of some products of the further action of chlorine. It retains also a small quantity of codeine, from which it is purified by dissolving in hydrochloric acid, boiling with animal charcoal and reprecipitating with ammonia; and it is finally obtained in crystals from its solution in boiling spirit.

In its general properties chlorocodeine closely resembles bromocodeine; so much so, indeed, that they may be easily confounded with one another. It is sparingly soluble in boiling water, and deposited, on cooling, in minute prisms, exactly similar to, and apparently isomorphous with, those of bromocodeine. It is readily soluble in strong alcohol, especially with heat, and sparingly soluble in æther. It dissolves in sulphuric acid in the cold without change,

but the solution is charred by heating. Nitric acid dissolves it, and the solution is decomposed by boiling, but not by any means so readily as codeine. Red fumes are evolved along with a peculiar and excessively pungent vapour.

Analysis gave the following results:—

	I.	II.			
Carbon	65·00	64·62	36 =	216	64·76
Hydrogen	6·22	6·08	20	20	5·99
Chlorine	..	10·32	1	35·5	10·64
Nitrogen	..	..	1	14	4·19
Oxygen	..	..	6	48	14·42

The crystallized base lost at 212°, 7·18–7·53 per cent. of water. The calculated number for 3 equivs. of water is 7·48 per cent.; and the formula of the crystallized base is therefore $C^{36}H^{20}ClNO^6 + 3HO$.

The salts of chlorocodeine are exactly similar in their properties to those of bromocodeine, so much so that I have not thought it necessary to examine more than one or two of them.

Hydrochlorate of Chlorocodeine crystallizes in groups of needles, readily soluble in water.

Sulphate of Chlorocodeine is deposited from its hot solution in radiated groups of short prisms, which dissolve abundantly in boiling water and alcohol. Dried at 212°, it gave—

Chlorocodeine	79·34	Base. =	333·5	79·63
Sulphuric acid	11·90	$HOSO^3$	49·0	11·75
Water	8·76	4HO	36·0	8·62

Platinochloride of Chlorocodeine is obtained in the usual way, as a pale yellow precipitate, scarcely soluble in water. Its analysis gave 40·30 C, 4·09 H, and 18·29 per cent. of platinum. The formula $C^{36}H^{20}Cl\,NO^6\,HCl\,PtCl^2$ requires 40·02 C, 3·89 H, and 18·28 platinum.

VII. *Action of Cyanogen on Codeine.*

Dicyanocodeine.—When a current of cyanogen is passed into a solution of codeine in the smallest possible quantity of alcohol, the gas is rapidly absorbed, and the fluid acquires, first a yellow, and by continued action a brown colour. If the solution be then left to itself for some time, the smell of cyanogen disappears, and is replaced by that of hydrocyanic acid, and crystals are gradually deposited. In order to obtain the new compound in sufficient quantity, it is best to keep up a continuous slow current of cyanogen, by which means crystals are deposited during the action in considerable abundance. These are collected on a filter, and washed with a small quantity of alcohol; and the filtrate, on being again exposed to the action of cyanogen, yields an additional quantity of crystals inferior in purity to those obtained in the first part of the operation. The product is purified by solution with the aid of heat, in a mixture of alcohol and æther, from which it is deposited in crystals, which are colourless or slightly yellow. Obtained in this way, however, they are apt to retain a small quantity of codeine; and it is therefore

advantageous to pass cyanogen into the mixture to be used for their solution, by which means the last traces of codeine are converted into the new compound.

The substance so obtained is a new base, to which I give the name of *dicyanocodeine*. It is soluble in boiling absolute alcohol, or a mixture of alcohol and æther, and is deposited on cooling in thin six-sided plates, with a brilliant lustre. It is difficultly soluble in water, but on the addition of alcohol it is dissolved; nothing however is deposited from the solution on standing, and by evaporation it is decomposed, and crystals of codeine are left behind. With hydrochloric acid it is converted into a crystalline salt, but decomposition takes place immediately; for on the addition of potash to the fluid, ammonia escapes; and if it be left for four-and-twenty hours, hydrocyanic acid is evolved. With sulphuric and oxalic acid it likewise gives somewhat sparingly soluble compounds, which decompose rapidly, with the evolution of ammonia and hydrocyanic acid. The crystals deposited from alcohol and æther are anhydrous. Their analysis gave the following results:—

Carbon	68·22	68·04	40 = 240	68·37
Hydrogen	5·93	6·17	21 21	5·97
Nitrogen	11·81	11·50	3 42	11·68
Oxygen	14·04	14·27	6 48	13·97

These results correspond exactly with the formula $C^{40}H^{21}N^{3}O^{6}$. The method of its formation, however, indicates unequivocally that its rational formula must be $C^{36}H^{21}NO^{6}2C^{2}N$, representing it as formed by 2 equivs. of cyanogen coupled with 1 of codeine, and belonging to the same class of compounds as cyaniline. It differs however from that substance in containing 2 equivs. of cyanogen; and, owing to this circumstance, I was at first inclined to take a different view of its constitution, and to consider it as the hydrocyanate of a cyanocodeine formed by substitution, and represented by the formula $C^{36}H^{20}CyNO^{6}+HCy$, according to which its formation could obviously be equally well explained; and I considered the evolution of hydrocyanic acid, by treating it with acids, as favourable to this view. Attentive observation however convinced me, that though hydrocyanic acid is always produced by heating it with strong acids, it is never evolved immediately, as it necessarily must be if it existed as such; but that it only makes its appearance after the lapse of some time, and that only as the result of an advanced decomposition; for long before it is observed, the addition of potash to the acid solution causes an abundant evolution of ammonia.

The ease with which dicyanocodeine is decomposed has prevented my examining any of its compounds. I attempted to prepare a platinum salt by rapid solution in hydrochloric acid, and precipitation by bichloride of platinum; but the instant the latter substance was added, evolution of hydrocyanic acid was observed, and the results obtained were, as might be expected, wholly incongruous

and unsatisfactory. The decompositions of dicyanocodeine evidently afford several different substances; but I have not attempted to follow them out, as their investigation seemed to present some difficulties, among which not the least was that of obtaining the base itself in sufficient quantity.

VIII. *Action of Alkalies on Codeine.*

Codeine, when treated at moderate temperatures with potash, yields more than one volatile base, according to the circumstances in which the experiment is made. I have found that similar results are obtained by the use of hydrate of potash, or of potash-lime, or soda-lime prepared in the usual way. The method employed in the experiment was to mix codeine with 4 or 5 times its weight of potash-lime or soda-lime, and introduce the mixture into a retort with a tubulated receiver, having a doubly-bent tube attached to its tubulature, the end of which passed into a small flask containing hydrochloric acid, in order to retain any of the very volatile base which might not be condensed in the receiver. The retort was introduced into an oil-bath, and kept at a uniform temperature of 250° F. As soon as this temperature is reached, a slight peculiar odour is observed, which soon becomes more powerful, and a small quantity of water, retaining the bases in solution, collects in the receiver. The decomposition at 250° however is excessively slow, and even after many days, bases are evolved apparently in undiminished quantity; but I retained the mixture steadily at this point, in hopes of obtaining the product free from ammonia, which my preliminary trials had shown to be produced at higher temperatures; but I found that even with this low heat it was evolved always in appreciable, and in some experiments even in considerable quantity. I therefore gradually raised the temperature to about 350°, when a larger quantity of base was obtained; and after the heat had been sustained for some time, small crystals made their appearance, which deposited themselves in a line round the retort, just above the level of the oil in the bath, but which soon rose into, and collected in the neck of the retort.

These crystals resemble benzoic acid in their external appearance, and are at first perfectly colourless, but soon acquire a brownish shade by exposure to light and air. They consist of a base, and rapidly restore the colour of reddened litmus. They are sparingly soluble in water, but readily in acids, and give a precipitate with bichloride of platinum. The quantity of this substance obtained was excessively minute; and though considerable quantities of codeine were operated upon, all that was obtained served only to make the few qualitative experiments now detailed.

The watery fluid which collected in the receiver possessed a pungent and peculiar smell; it restored the colour of reddened litmus with great rapidity, and gave abundant fumes with hydrochloric acid. On the addition of solid potash, a highly volatile and pungent oily base collected as a layer on the surface of the fluid, and at the

same time a gaseous base escaped along with ammonia. From the small quantity of these substances which I was able to obtain, I could not attempt to prepare either of them in a pure state. I was therefore under the necessity of determining their constitution by the analysis of their platinum salts, which can be separated from one another, though not without difficulty. In order to prepare these salts, the basic fluid was saturated with hydrochloric acid, and evaporated to dryness in the water-bath, when it left behind a beautifully crystalline mass, highly soluble in water and deliquescent in moist air. This was dissolved in absolute alcohol, to separate ammonia, and the filtered solution mixed with an alcoholic solution of bichloride of platinum, when the platinum salts were immediately thrown down as a pale yellow powder, very sparingly soluble in absolute alcohol, but readily dissolved on the addition of water. The separation of the two bases is best effected by heating the washed precipitate with boiling absolute alcohol, and adding water in small quantities until the whole is dissolved. The crystals which deposit on cooling are one of the salts in a state of purity, if the process have been properly managed; or, at all events, only require a repetition of the process to make them absolutely pure. The salt thus obtained is scarcely soluble in absolute alcohol or æther, but is readily soluble in water and dilute spirit, and is thrown down from the latter solution by æther in the form of fine yellow scales. Its analysis gave the following results:—

	I.	II.			
Carbon.....	5·48	..	2 =	12	5·06
Hydrogen	2·66	..	6	6	2·52
Nitrogen	..	..	1	14	5·90
Chlorine	..	..	3	106·5	44·91
Platinum.....	41·49	41·32	1	98·7	41·61

The formula of the salt is therefore $C^2 H^5 N, HClPtCl^2$; and the base is consequently the methylamine of Wurtz, with whose description of that substance and its platinum salt it perfectly agrees.

The preparation of the platinum salt of the other base was attended with much greater difficulty, and I did not succeed in obtaining it quite free from methylamine. In order to obtain it, the fluid which had deposited the methylamine salt was evaporated to a small bulk, the salt which separated filtered off, and æther added to the mother-liquor. Immediately a precipitate is obtained, generally in the form of minute yellow needles, but sometimes in scales. It is sparingly soluble in alcohol and æther, and highly soluble in water, from which it crystallizes in long needles, and with such facility that a few drops evaporated on a watch-glass leave the salt they contain in the form of five or six needles crossing the whole space occupied by the solution. The quantity of this salt which I had at my disposal was too small to admit of my carrying its purification by recrystallization as far as was to be desired, and consequently a small quantity of methylamine remained in those subjected to analysis:—

	I.	II.			
Carbon	12·27	..	6 =	36	13·57
Hydrogen.....	3·62	..	10	10	3·77
Nitrogen	..	..	1	14	5·27
Chlorine	..	..	3	106·5	40·18
Platinum	37·71	37·56	1	98·7	37·21

These results approach most closely to the formula $C^6 H^9 N, HCl PtCl^2$; and though the carbon is very deficient and the platinum considerably in excess, there can be no doubt that this is due to the imperfect separation of the methylamine, and that this is its true formula, and that of the base itself $C^6 H^9 N$. The base then obviously belongs to the same series as methylamine, and forms the term of the series corresponding to metacetonic acid, and in accordance with the system of nomenclature adopted by Wurtz it receives the name of metacetamine. I have not attempted the examination of the salts of this base, as I did not obtain it in sufficient quantity for that purpose; but I take the opportunity of stating, that before I had obtained it from codeine, I had ascertained its existence among the products of destructive distillation of animal substances, and that I shall, at a future period, detail the properties of its compounds*.

The residue in the retort after these bases have been evolved is dark cinnamon-brown, and slightly coherent; it dissolves in water, with a dark brown, almost black colour, and gives with acids a flocculent brown precipitate of a humus-like substance, and perfectly amorphous, which I have not thought it necessary to examine. It still contains nitrogen; and by exposure to a heat gradually raised to low redness, it gives an additional quantity of volatile bases, among which ammonia becomes more and more abundant as the temperature rises. A non-basic oil also makes its appearance, but only in very small quantity.

Since these experiments were made, I have received the February number of the 'Annalen der Chemie und Pharmacie,' which contains a preliminary notice of an investigation by Wertheim of the action of soda-lime on certain organic bases. He has obtained metacetamine from narcotine, and methylamine from morphia; and considering these substances to be directly eliminated from the bases, he expects to obtain the residual atoms in the form of a definite compound. I entertained a similar idea with regard to codeine, until I detected the formation of two different bases, which seemed to me rather to indicate that these substances appear as the result

* I may at the same time mention, that I have convinced myself that the petinine described by me two years since as existing in bone-oil is represented by the formula $C^8 H^{11} N$, and not by $C^8 H^{10} N$, which I then gave for it. Indeed my analysis of the platinum salt, which is most to be depended upon, tallies equally well with either formula. I have also ascertained the existence of ethylamine and methylamine in bone-oil. The details of these experiments will be contained in the second part of my paper "On the Products of the Destructive Distillation of Animal Matters."

of a true destructive distillation, and that possibly, by varying the circumstances of the experiment, other bases may be obtained.

I have also observed another remarkable decomposition of codeine, by which volatile bases are obtained. I have already mentioned the formation, by the action of nitric acid, of a resinous acid, with the examination of which I am still engaged. This acid, which is insoluble in water, dissolves readily in dilute potash, with a red colour; and the solution on boiling evolves a volatile base in great abundance. I have not yet determined the whole circumstances under which this change takes place, but reserve this for a future communication*.

I have likewise examined the action of iodine on codeine, which yields a magnificent crystalline compound, presenting the phænomena of pleochroism in a remarkable manner. Difficulties connected with the analysis have however prevented my hitherto completing its investigation.

On Benzhydrole, a new Stearoptene from Oil of Cassia.

By F. Rochleder *and* Dr. H. Hlasiwetz.

The authors examined the stearoptene from oil of Cassia, which in the crude state consisted of transparent, colourless, and in part yellow crystalline fragments of considerable size, coated with a yellow-brown oil, smelling strongly of cinnamon. The pure substance the authors call benzhydrole. To obtain it in a pure state, the fragments were dissolved in the smallest possible quantity of hot absolute alcohol. On cooling, the liquid solidified to a yellow laminar crystalline mass, which was pressed between blotting-paper, and several times recrystallized from absolute alcohol.

Benzhydrole, $C^{28}H^{15}O^{5}$, is colourless, inodorous, crystallizes in laminæ of a strong lustre, is brittle and easily reduced to powder, grates between the teeth, melts readily, and is coloured by heat, becoming yellow soon after melting. In the melted state it forms a colourless highly refractive oil. Heated in a small retort, it creeps up the sides, and distils over without boiling. The distillate is a yellow oil, which soon congeals to a solid mass, of laminar structure and of a yellow colour, owing to partial decomposition. This substance dissolves in sulphuric acid with a full yellow colour, and is again precipitated by water. On analysis, the melted substance furnished—

Carbon	75·35	75·00	75·24	28	=2100·0	75·33
Hydrogen	6·86	6·80	6·83	15	187·5	6·72
Oxygen	17·79	18·20	17·93	5	500·0	17·95

When benzhydrole is boiled with a solution of caustic potash in a vessel which is connected with an apparatus for condensing the

* The action of nitric acid on the organic alkalies, in this point of view, is now under investigation in my laboratory. Narcotine has been found to undergo a precisely similar change, yielding a compound which gives off a volatile base by ebullition with potash, and a whole series of other substances, the constitution of which will be detailed so soon as the investigations are completed.

volatile products, a turbid water and drops of a heavy oil are obtained. The oil, which sinks in the water, is of a light yellow colour, and has the agreeable odour of an emulsion of sweet almonds. In order that the reaction might be complete, the product was again mixed with solution of potash and distilled. The volatile oily product was dried over chloride of calcium, rectified, and then analysed. It gave—

Carbon	69·66	69·60	42 =	3150·0	69·61
Hydrogen	6·05	6·32	22	275·0	6·08
Oxygen	24·29	24·08	11	1100·0	24·31

In the action of the potash and the atmosphere upon benzhydrole, there is formed along with the above product a small quantity of a brown viscous resin, which remains with the potash.

When mixed with nitric acid, benzhydrole instantly becomes yellow, even when the acid is dilute; it melts to an oil which floats on the nitric acid. When concentrated acid and heat are employed, a violent reaction ensues. When this is over, the liquid is evaporated at a gentle heat, in a shallow dish, until the liquid solidifies on cooling. It is dissolved in water, the boiling-hot yellow solution filtered from some flakes of resin, and set aside to cool. A large quantity of minute yellowish crystals separate, which are collected upon a filter, washed with cold, and recrystallized from boiling water. After frequent recrystallization, the acid is pure, colourless, and possesses all the properties of nitrobenzoic acid. Like that acid, it precipitates persalts of iron, and melts under water to an oil when there is not sufficient of it for solution. With zinc and muriatic acid, the hot solution of the acid becomes transitorily copper-red, like nitrospirolic acid; with solution of caustic potash, it turns dark orange-red, and colours a large amount of water yellow. When heated with soda-lime, it gives off ammonia. Analysis proved that it corresponded to the composition of nitrobenzoic acid with 1 equiv. of water $= C^{14}(H^4NO^4)O^3 + 2HO + Aq$:—

Carbon	45·48	14 =	1050·0	45·40
Hydrogen	3·95	7	87·5	3·78
Oxygen	..	10	1000·0	
Nitrogen	..	1	175·0	

Proc. of the Acad. of Vienna, June 1850, p. 1.

√ *Researches on Cinchonine. By* Dr. Hlasiwetz.

The author has obtained two essentially different bodies in the fractional crystallization of commercial cinchonine, the first of which has all the properties generally attributed to cinchonine. It crystallizes in moderately large shining prisms, is tolerably soluble in alcohol, furnishes quinoidine when heated, and sublimes in part to a matted tissue of fine crystals. When sublimed in a current of ammonia or hydrogen, remarkably brilliant prisms, more than an inch long, are obtained. This substance possessed exactly the com-

position required by Regnault's formula, $C^{40}H^{24}N^2O^2$. The sublimed acicular crystals have the same formula.

The second substance, which is obtained by successive crystallization, separates from the alcoholic mother-liquor of the cinchonine in beautiful hard rhomboidal crystals, which may be obtained of very considerable size and diamond lustre from æther, in which they dissolve very readily, which is not the case with cinchonine.

These crystals become opake when heated, melt, and on cooling solidify to an amorphous mass, and furnish, neither alone nor in a current of ammonia or hydrogen, a trace of crystals.

The analyses of this substance and of its platinum salt led to the formula $C^{20}H^{12}NO^2$, which is the composition of the so-called β-quinine detected by Heijningen in commercial quinoidine. The author calls it *cinchotine*.

Commercial cinchonine moreover contains a tolerable amount of a brown basic resin, which was not further examined by the author, but which appeared to be quinoidine. In a sample of beautifully-crystallized cinchonine from Merk's establishment in Darmstadt, the author found the composition to agree with the formula which Liebig first proposed, $C^{20}H^{11}NO$. From this he concludes that neither Liebig's formula nor that of Regnault should give way for that recently advanced by Laurent, as they actually represent certain kinds of cinchonine. The author has never been able to obtain Laurent's most recent formula with pure cinchonine; according to a series of most careful analyses, he constantly found numbers which led only to the formula $C^{40}H^{24}N^2O^2$. The platinum salt places this formula beyond doubt, and proves at the same time that it should be halved, and written $C^{20}H^{12}NO$.

In some attempts to oxidize cinchonine by various agents, the author always reobtained pure cinchonine. The cinchonine reobtained was in every case submitted to analysis. In the treatment with chlorine, with manganese and sulphuric acid, with permanganate of potash, with nitric acid, with chloride of phosphorus, further after ebullition with an acid solution of bichloride of platinum and fermentation with emulsine, the cinchonine comes out unaltered, or a resinous mass is obtained, as in the treatment with chlorine, from the solution of which pure cinchonine was precipitated by ammonia. The results of the analyses of such different samples all correspond to the formula $C^{20}H^{12}NO$, and are as follows:—

	I.	II.	III.	IV.	V.
Carbon.....	77·78	77·75	78·24	78·15	78·06
Hydrogen ..	7·72	7·80	7·73	7·75	7·67
	VI.	VII.	VIII.	IX.	X.
Carbon.....	78·15	78·15	78·24	78·08	77·57
Hydrogen ..	7·62	7·64	7·73	7·28	7·65

When a solution of cinchonine in alcohol acidulated with muriatic acid is precipitated with bichloride of platinum, a crystalline precipitate of a light yellow, at first almost white colour, is obtained. This yields on analysis numbers which only accord with Laurent's formula, $C^{38}H^{22}N^2O^2$, so as to lead to the supposition that in the treatment with bichloride of platinum, C^2H^2 had been eliminated in

one form or the other. Experiments in this direction however showed nothing of the sort; on the contrary, it was found that in order to obtain a platinum salt corresponding to the formula $C^{20} H^{12} N O$, the first precipitate of the cinchonine with bichloride of platinum must be redissolved in water, which requires very long ebullition. On cooling, a whitish pulverulent precipitate first makes its appearance, and after long standing, a dark orange-yellow, very beautifully crystallized platinum salt separates, which had the following composition:—

Carbon	33·1	..	20	33·3
Hydrogen	3·6	..	12	3·3
Nitrogen	..	..	1	
Oxygen	..	..	1	
Platinum	27·38	27·34	1	27·36
Chlorine.....	..	..	2	

The alkaloid separated from this platinum salt by sulphuretted hydrogen gave, after recrystallization, on analysis, numbers agreeing with the preceding:—

Carbon	77·83	20	77·92
Hydrogen	7·65	12	7·79

The cinchonines of commerce are very variable preparations. Besides the one which contained β-quinine, the author analysed a beautifully white crystallized cinchonine, which was mixed with a mere trace of amorphous powder. It furnished—

	I.	II.
Carbon	67·04	67·11
Hydrogen	7·42	7·58

This consequently contained much less carbon. It was dissolved in dilute muriatic acid, precipitated with ammonia; the precipitate, after being washed, recrystallized from alcohol, and analysed, was found to have the composition $C^{20} H^{12} NO$. Laurent's statements appear to be founded on a cinchonine which possibly contained a small quantity of β-cinchonine, the carbon in which is 4 per cent. less, very little of which therefore would suffice to lower the carbon equivalents in the formula.

Of the formulæ hitherto proposed for cinchonine, that of Regnault agrees best with the author's analyses; they however lead more correctly to the formula $C^{40} H^{23} N^2 O^2$, which requires C 78·18, H 7·49, N 9·12, O 5·21. The platinum double salt likewise corresponds with this, $C^{40} H^{23} N^2 O^2 + Cl^2 H^2 + Pt^2 Cl^4$.

Carbon.....	33·1	..	40	33·38
Hydrogen ..	3·6	..	25	3·48
Nitrogen	..	..	2	
Oxygen	..	..	2	
Chlorine	..	..	6	
Platinum	27·38	27·34	2	27·42

That in this formula there are 2 equivs. of bichloride of platinum to 1 of cinchonine, may, according to the author, be explained by the fact, that the salt is only formed upon the addition of HCl.—*Proc. Imp. Acad. Vienna*, 1850.

Researches on Phenole (Hydrate of Phenyle). *By* A. Cahours.

On distilling crystallized anisic acid with an excess of caustic baryta or lime at a dark red heat, this body is decomposed into carbonic acid, which remains with the base, and a ternary volatile product, anisole, which only differs from phenole by C^2H^2. I subsequently found that salicylate of methylene, which exhibits the most perfect isomerism with anisic acid, but which possesses very different properties, furnished under the same circumstances anisole entirely identical with that formed by the decomposition of anisic acid.

The production of anisole from salicylate of methylene, a compound which may be regarded as salicylic acid which has exchanged an equivalent of hydrogen for an equivalent of the body C^2H^3, led me to admit some years ago that anisole might possibly be methylated phenole (*phénole méthylé*), that is to say, phenole which has exchanged H for C^2H^3, and whose molecule should therefore be represented by the formula $C^{12}H^5O^2$, $C^2H^3 = C^{14}H^8O^2$.

Salicylic æther also furnishes, under the influence of heat and bases, a ternary compound homologous with anisole, which I have called *phenetole*, and which may be represented by $C^{12}H^5O^2$, $C^4H^5 = C^{16}H^{10}O^2$. Now it may be asked, are anisole and phenetole, which differ by C^2H^2 and $2C^2H^2$ from phenole, homologous with that body; or are they merely cases of isomerism of the true homologues of the latter? When the different known alcohols are acted upon by formic acid, we obtain a series of compounds known under the names of formiomethylic, formethylic and formioamylic æthers, whose composition may be represented by the following formulæ:—

$C^2H^2O^4$, formic acid..... = 4 vols. vapour.
C^2HO^4, $C^2H^3 = C^4H^4O^4$, formiomethylic æther = „ „
C^2HO^4, $C^4H^5 = C^6H^6O^4$, formic æther ..... = „ „
C^2HO^4, $C^{10}H^{11} = C^{12}H^{12}O^4$, formioamylic æther = „ „

These compounds differ therefore from formic acid only by C^2H^2, $2C^2H^2$, $5C^2H^2$, and exhibit a perfect isomerism with acetic, propionic and caproic acids. Now these alone are the true homologues of formic acid, for they fulfil the same chemical functions as the latter, which is not the case as regards the preceding compounds. I imagined the same might be the case with respect to anisole and phenetole, which offer no analogy with phenole as regards their properties; and that these bodies would stand in the same relation to the latter as the formiate of methylene and formic æther to formic acid.

With a view to solve this question, I followed the method recently employed by Prof. Williamson, and acted with iodide of methyle and iodide of æthyle upon potash-phenole in sealed tubes heated to 212–248°; the reaction is soon finished, and some compounds are obtained which exhibit the most perfect identity with anisole and phenetole. I have obtained the same results by distilling potash-phenole with sulphomethylate and sulphovinate of potash.

By substituting for the iodides of methyle and æthyle iodide of amyle, I obtained a new compound analogous to the preceding; I shall call it *phenamylole*; it forms a colourless limpid oil, lighter

than water, having an agreeable aromatic odour, and boiling between 435° and 437°. Its analysis led to the formula $C^{22}H^{16}O^2 = C^{12}H^5O^2$, $C^{10}H^{11}$. Nitric acid acts upon it most violently, and converts it into a heavy oil, which on treatment with an alcoholic solution of hydrosulphate of ammonia, furnishes a crystalline base, forming crystallizable salts. I have named the latter, which is homologous with nitroanisidine, *nitrophenamylidine*.

Concentrated sulphuric acid dissolves it, assuming a red colour. Water added to the liquid gives no precipitate. On treatment with carbonate of baryta and evaporation, it yields a crystallized salt.

The formation of anisole, phenetole, and phenamylole, by the reciprocal action of the iodides of methyle, æthyle, amyle and potash-phenole, places the true constitution of these bodies beyond all doubt; they are evidently to phenole what the different compound æthers are to their corresponding acids, whatever hypothesis be adopted regarding their constitution.

The preceding researches confirm therefore the hypothesis I advanced some years ago relatively to the constitution of anisole and phenetole, compounds which I regarded as phenic æthers.

In conclusion, I may mention, that by acting with chloride of benzoyle upon salicylole (hydruret of salicyle), I obtained a compound in brilliant quadrilateral prisms, which fuse at a slightly elevated temperature into a colourless liquid, and sublime when heated further into acicular crystals; it has the composition and properties of parasalicyle. Its formation may be expressed by the equation—

$$C^{14}H^5ClO^2 + C^{14}H^6O^4 = ClH + C^{28}H^{10}O^6.$$

Comptes Rendus, Jan. 13, 1851.

ANALYTICAL CHEMISTRY.

On the Separation of the Alkalies from Magnesia, and on the Analysis of the Alkaliferous Minerals. By M. Ebelmen.

The separation of magnesia from the alkalies is one of the most delicate operations of chemical analysis. It has generally to be done towards the end of the analysis; and in the case of those silicates which have to be decomposed by hydrofluoric acid, it is nearly always in the state of sulphates that the three bases which have to be separated occur. It is usual to separate the magnesia, and to convert the potash and soda into chlorides, in order to estimate the potash as platino-chloride of potassium.

The plan generally followed for this purpose is the one proposed by Berzelius. The sulphates, dissolved in water, are treated with an excess of acetate of baryta. The filtered liquid is evaporated to dryness and the residue calcined, in order to change the acetates into carbonates. On treatment with boiling water, only the carbonates of potash and soda are dissolved, leaving the magnesia and carbonate of baryta, which are separated by dissolving them in hydrochloric acid, precipitating the baryta by sulphuric acid, and then evaporating the filtered liquid to dryness, in order to estimate

the magnesia as sulphate. As regards the alkaline carbonates, they are converted into chlorides, and the potash separated by chloride of platinum.

I have employed this process in the analysis of a large number of alkaliferous rocks; it is very tedious; and, moreover, the sulphate of baryta, which proceeds from the precipitation by the acetate, filters very slowly, and the liquid constantly passes turbid, even when it is heated and acetic acid is added to it. Consequently, on calcining the product of evaporation and then treating the substance with water, the alkaline carbonates contain a certain amount of sulphates, which interferes with the accuracy of the determinations and the separation of the potash by chloride of platinum.

I first tried to simplify the operation and to render it more accurate, by adding prepared carbonate of baryta to the solution of the sulphates of magnesia, potash and soda. I found that the carbonate of baryta completely separated the magnesia in a warm liquid, but that it did not wholly convert the alkaline sulphates into carbonates. There always remains in the liquid, however large the excess of carbonate of baryta, the state of dilution or the temperature of the liquid, an appreciable quantity of sulphuric acid. This fact is readily explained, as we know that the alkaline carbonates in solution have the property of decomposing the insoluble sulphates, as those of baryta and strontia, more or less completely according to the relative proportions of carbonate and sulphate present. It will therefore be readily conceived that the presence of a certain quantity of alkaline carbonate formed by the reaction of the carbonate of baryta on the soluble sulphate, will prevent the total decomposition of the alkaline sulphate.

But if the solution of the sulphates be acted upon simultaneously by carbonate of baryta and a current of carbonic acid, a period soon arrives when the liquid contains baryta in solution in the state of bicarbonate, and not a trace of sulphuric acid. The alkalies are then completely changed into bicarbonates, and are present in the liquid with a small quantity of the bicarbonates of magnesia and baryta. They are easily separated by filtering the liquid, evaporating to dryness at a pretty high temperature, in order to reduce the whole to the state of neutral carbonates, then treating the residue with a very small quantity of boiling water, which dissolves the alkaline carbonates, but no magnesia or baryta.

It is readily ascertained whether enough carbonic acid has been passed into the alkaline liquid. A few drops are filtered, and tested with 1 drop of extremely weak sulphuric acid; if the liquid become turbid, we may be sure it contains no more sulphate. The few drops which had been removed are reunited with the principal liquid, and the whole filtered.

The employment of the carbonate of baryta has this other advantage over the acetate, that the product of the evaporation not being very bulky, requires but a very small quantity of water to dissolve completely the alkaline carbonates without taking up any appreciable quantity of baryta or magnesia; it is very different when the acetate is used. The product of the calcination usually contains

much carbonate of baryta; a somewhat large quantity of water is required to wash it completely, and some of the magnesia is dissolved.

To test the accuracy of the method I have described, I made the following experiments:—

1. I dissolved in water—

Crystallized sulphate of potash heated to redness.. 0·547 grm.
Crystallized sulphate of magnesia..... 1·930 ...

I added about 200 cub. centim. of water and 10 grms. of carbonate of baryta obtained by precipitating the chloride of barium with carbonate of ammonia, washing with care, and drying the precipitate at a gentle heat. The liquid was boiled and allowed to cool, at the same time passing through it a current of carbonic acid until it was rendered turbid by the addition of 1 drop of very dilute sulphuric acid. It was filtered, evaporated, the residue heated to a dark red, then treated with a small quantity of boiling water and filtered. The alkaline carbonate was saturated with hydrochloric acid, when there was obtained—

Dry chloride of potassium ..... 0·4640
There ought to have been obtained according to theory 0·4677
(S=200, K=487·5, Cl=443·5).

The loss therefore amounted to 0·0037 grm., or merely 0·8 per cent. The chloride obtained dissolved entirely in water, except a few imponderable flocculi. The liquid was not precipitated by sulphuric acid, by chloride of barium, nor by phosphate of soda and ammonia.

2. I mixed, as in the preceding experiment—

Sulphate of soda obtained from .. 0·515 of dry chloride of sodium
Crystallized sulphate of magnesia.. 1·260
Dry carbonate of baryta..... 10·000

I obtained—

Dry chloride of sodium ..... 0·508
Loss ..... 0·007, or 1·4 per cent.

The chloride of sodium was absolutely pure; it contained neither sulphuric acid, magnesia nor baryta. These two experiments show the accuracy of the process, as the alkalies were obtained in the state of very pure chlorides and with scarcely an appreciable loss.

I have sought to apply the same process to the analysis of those minerals which are not attacked by acids of moderate strength.

In the analysis of a silicate which is not decomposed by hydrochloric acid, the analysis is generally divided into two distinct operations. In the one, the mineral is attacked by alkalies in a silver crucible, or by the alkaline carbonates in a platinum crucible; the fused mass treated with hydrochloric acid, and the silica and the other bases, excepting the alkalies, successively separated. To determine the amount of alkalies, it is necessary to decompose the mineral, either with carbonate of baryta by the dry way, or by hydrofluoric acid. In both cases the bases are obtained as sulphates, as in the first case the baryta has to be removed by sulphuric acid, and in the second the hydrofluoric acid has to be expelled also by sulphuric acid. The liquid is then successively precipitated by ammonia, the hydrosulphate and the oxalate of ammonia then evapo-

rated, and the residue strongly calcined to expel the ammoniacal salts. A mixture of the sulphates of the alkalies and sulphate of magnesia is obtained, which might be separated in the manner above described. However, the decomposition of the sulphate of ammonia by heat is very tedious, and it is difficult to avoid projections, and the loss which thence results.

I imagined that the determination of the alkalies might be much simplified by operating in the following manner:—The silicate is treated in a similar manner with hydrofluoric and then with sulphuric acid; the solution of the sulphates is treated directly with carbonate of baryta and carbonic acid. When the sulphuric acid is entirely precipitated, the liquid is filtered, and the solution of the alkaline bicarbonates evaporated to dryness as above described. The experiments made to verify the accuracy of this method, however, show that the whole amount of the alkalies is not obtained; when the alumina is precipitated by carbonate of baryta, a considerable portion is retained by the precipitate; in one experiment the loss amounted to more than a tenth. Far more satisfactory results are obtained when ammonia, and the carbonate of ammonia and the carbonate of baryta are used successively. The liquid containing all the bases in the state of sulphates, is precipitated by ammonia or the carbonate. The alumina is precipitated with the peroxide of iron and a portion of the manganese and magnesia. It is filtered, and the liquid boiled with an excess of carbonate of baryta, which completely decomposes the sulphate of ammonia. When the addition of a fresh quantity of carbonate of baryta no longer produces a disengagement of carbonate of ammonia, the liquid is treated with carbonic acid. In this manner we avoid decomposing the sulphate of ammonia by calcination. The determination of the alkalies is then more simple and exact.

The following are the results obtained in two experiments made to verify this method. I took—

Alumina	0·50	0·50
Dry sulphate of potash	0·50	0·50
Crystallized sulphate of magnesia	0·00	1·50

The alumina was treated with concentrated sulphuric acid, the sulphate evaporated to dryness, redissolved in boiling water, the other sulphates added to it, and the liquid precipitated with an excess of carbonate of ammonia. The gelatinous precipitate was collected on a filter and washed, the liquid was boiled to expel the excess of carbonate of ammonia, then carbonate of baryta added as long as any smell of ammonia was perceptible. The cold liquid was then treated with carbonic acid, when it furnished—

Pure chloride of potassium	0·419	0·422
Theory gives	0·4275	0·4275
Loss	0·0085	0·0055
Per cent.	2·0	1·3

It will be seen that the differences between the results of the experiment and those which ought to have been obtained are not considerable, and in the right direction. I think this method may be employed in the analysis of silicates and of alkaliferous rocks. I

have employed it in the analysis of several rocks used in the manufacture of porcelain in China, and the results it has furnished are most satisfactory.—*Ann. de Chim. et de Phys.*, Nov. 1850.

√ *Process for determining the Amount of Prussic Acid in the Medicinal Prussic Acid, Bitter Almond and Cherry-Laurel Waters.* By Prof. J. Liebig.

When a solution of caustic potash is added to a liquid containing prussic acid until it has a strong alkaline reaction, and a dilute solution of nitrate of silver is then slowly poured into it, a precipitate is formed, which on agitation immediately disappears again to a certain limit. When the prussic acid is mixed with a solution of caustic potash and a few drops of chloride of sodium, and then the solution of silver added, a certain proportion of the latter may be added as in the previous case before a permanent precipitate forms, which in this case is white chloride of silver.

The liquid containing prussic acid, when mixed with potash, contains cyanide of potassium, in which the oxide or chloride of silver are soluble, until the well-known double compound, consisting of equal equivalents of cyanide of potassium and cyanide of silver, is formed, and which is not decomposed by excess of potash. When therefore the amount of silver in the solution is known, and at the same time how much of it in volume or weight has been added to the alkaline liquid containing the prussic acid until the formation of a precipitate, we can thence determine the amount of cyanogen or prussic acid in the liquid, for 1 equiv. of consumed silver exactly corresponds to 2 equivs. of prussic acid.

The following experiments by Dr. Fleitmann will show the accuracy of the method. In the first place, the amount of prussic acid in a very dilute solution was determined directly by precipitation with nitrate of silver; 100 cub. centim. of this prussic acid furnished 0·332 grm. cyanide of silver, corresponding to 0·067 per cent. of acid. The same solution required for the complete precipitation of a normal liquid containing in 100 cub. centim. $\frac{1}{2}$ a grm. of metallic silver, 53·5 cub. centim. 100 cub. centim. of the same prussic acid, mixed with potash, and then constantly shaken with the same solution of silver until the appearance of a milkiness, required 27 cub. centim. 150 cub. centim. of the same prussic acid required 40 cub. centim. of the silver solution; according to these experiments the liquid contained—

		By a measured quantity of normal liquid in		
		alkaline solution.		
	By direct determination.	I.	II.	acid solution.
Prussic acid	0·067 p. c.	0·068	0·067	0·067

Similar results were obtained by M. Fabre.

It follows from these experiments, that the method of determining the amount of prussic acid in an alkaline liquid by means of a normal solution of silver is as trustworthy and accurate as any of the

best methods hitherto employed; whilst in several other respects, for instance the ease and quickness with which the experiment is made, it far surpasses them.

The presence of formic acid or hydrochloric acid in the prussic acid, which would render the determination of its amount by a normal solution of silver inaccurate, has not the slightest influence on its estimation in the alkaline liquid; and it has moreover the advantage, that as soon as the reaction becomes perceptible the operation is terminated, in which it is preferable to similar methods the completion of which depends on the cessation of the reaction. In the estimation in the alkaline liquid, both liquids that are mixed remain clear; as soon as the slightest permanent milkiness is perceptible, the analysis is finished, and to arrive at this point one or two minutes suffice. In ascertaining the quantity directly by nitrate of silver, a precipitate is formed, which renders the liquid turbid; towards the end of the operation it is necessary to wait until this has subsided and the liquid again become clear, in order to determine when no further precipitation occurs. Now with the dilute liquid the last traces of cyanide of silver settle with much greater difficulty than in the estimation of chlorine; and it is precisely owing to this circumstance that the method is disagreeable and tedious.

Aqueous prussic acid is so rarely employed for medicinal purposes, that a test for that is scarcely required; but the distilled waters of bitter almonds and of cherry-laurel, both of which contain prussic acid, are in daily use; and it is highly desirable that the amount of the active ingredient should, under certain circumstances, be ascertained with accuracy; the process described answers admirably for the purpose.

In general, cherry-laurel water is clear and transparent; the water of bitter almonds, on the contrary, is usually milky from the presence of little drops of oil; and it is requisite to mix the latter with 3 to 4 times its bulk of water to render it clear, otherwise the termination of the reaction is not seen distinctly.

The method described may also serve to test the commercial cyanide of potassium; and by its means I have unexpectedly found that the cyanide prepared according to the method described by me contains a comparatively small amount of cyanide of potassium. Two samples from two different preparations were examined; the one furnished 63·5 per cent., the other only 59·99 per cent. of cyanide of potassium.—Liebig's *Annalen*, Jan. 1851.

On the Determination of the Value of Barks by means of Chloroform. By M. Rabourdin.

I shall attempt to show in this paper, how the amount of the alkaloids may be determined in the cinchonas, by turning to account the property which chloroform possesses of taking up these substances from an aqueous solution.

Examination of the Gray Barks.—40 grms. of the gray bark of commerce, reduced to powder and passed through a close hair-sieve,

are moistened with a sufficient quantity of water acidulated with hydrochloric acid (20 grms. of acid to 1000 grms. of water), and placed in a small cylindrical tube. A piece of filtering paper is placed beneath, and the powder is washed with acidulated water. When the liquid which passes is nearly colourless and free from bitterness (if the powder is uniformly and suitably stratified, it is exhausted when from 200 to 250 grms. of liquid have been collected), no more liquid is poured over it; to the collected liquid from 5 to 6 grms. of caustic potash and 15 grms. of chloroform are added; the whole is well shaken for a few minutes, and set aside; in the course of half an hour the chloroform is deposited, carrying down with it the whole of the cinchonine. The supernatant transparent red liquid is carefully decanted; the deposit, after being well washed with water by decantation, is emptied into a porcelain capsule. This deposit is composed of a liquid portion, which is a solution of cinchonine in chloroform, of a semisolid reddish portion, consisting of cinchonine, a mixture of chloroform and cinchona-red. The capsule is placed on a bath of boiling water, to expel the chloroform, and the residue treated with water containing some hydrochloric acid, which dissolves the whole of the cinchonine and a part of the cinchona-red. It is filtered, and ammonia, diluted with 15 to 20 times its bulk of water, added to the liquid drop by drop, each time stirring well. As soon as a white cloud appears which no longer dissolves on being agitated, no further addition is made. The object of this operation is to precipitate the cinchona-red without touching the cinchonine. The moment to stop is readily ascertained, as the cinchona-red is precipitated in reddish-brown, the cinchonine, on the contrary, in curdy-white flakes. After a sufficient quantity of dilute ammonia has been added, the liquid, which should be colourless, is filtered, the filter washed with a little distilled water, and the united liquids precipitated by an excess of ammonia. The precipitate, which is pure cinchonine, is collected, dried and weighed.

In one experiment I found 0·19 grm., and in a second 0·195 cinchonine; taking the highest number, we have 4·87 grms. of alkaloid in 1 kilogrm. of gray bark.

Examination of the Yellow Barks.—It is not necessary to operate upon more than 20 grms. of the bark of the yellow cinchona. The bark is powdered, passed through a sieve, and exhausted with acidulated water; from 150 to 200 grms. of liquid are obtained, to which are added 5 to 6 grms. of caustic potash and 10 grms. of chloroform. The mixture is well shaken, then set aside. A very heavy whitish deposit, consisting of quinine, cinchonine and chloroform, takes place; sometimes the separation is complete and instantaneous. The transparent, red, supernatant liquid is decanted, the chloroformic solution washed, and collected in a small capsule, when, on the spontaneous evaporation of the chloroform, the alkaloids are left in a pure state.

The red barks behave precisely like the yellow ones. What has been stated of the latter applies equally to them.—*Comptes Rendus*, Dec. 2, 1850.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Further Observations on Caffeine. *By* Dr. F. R. Rochleder.

When a thick paste of caffeine and water is treated with chlorine, the caffeine gradually disappears. According as the action of the chlorine has continued for a longer or shorter time, and the current of gas been quick or slow, in which first case the liquid becomes heated to 122° F., either the whole of the caffeine is decomposed, or a part still remains unaltered, and the liquid contains a mixture of different substances. (See Chem. Gaz., vol. vii. pp. 109, 457, and vol. viii. pp. 133, 152.)

One of these products, the *chlorocaffeine* of the author, is only contained in the liquid when the action of the chlorine has been discontinued before the whole of the caffeine is decomposed. *Amalic acid*, a second product, is contained in the solution along with chlorocaffeine when the action of the chlorine has been but of short duration, and with *cholestrophane*, which is formed from the amalic acid by oxidation, when the current has been continued longer.

Besides these substances, the liquid contains *hydrochlorate of methylamine*. When the liquid obtained by passing chlorine into a paste of water and caffeine is evaporated on the water-bath, chlorine, muriatic acid and a substance which smells of chloride of cyanogen, and brings tears into the eyes, escapes, and small colourless granular crystals separate, the quantity of which constantly increases. When there is no longer a further deposit of these crystals, the liquid is frequently stirred while cooling, and filtered from the crystals, which are impure amalic acid. When the action of the chlorine has been but of short duration, the chlorocaffeine separates directly after, or with the last traces of amalic acid, in white light flakes and crusts. When the solution is filtered from this impure chlorocaffeine, and further evaporated on the water-bath, during which operation muriatic acid is constantly given off, a reddish-yellow syrup remains, which concretes on cooling. This mass is pressed between folds of fine linen; an almost colourless crystalline mass is obtained, and a reddish-yellow fluid of the consistence of honey; the crystalline mass is impure cholestrophane; the thick liquid contains hydrochlorate of methylamine.

Chlorocaffeine, $C^{16} H^9 Cl, N^4 O^4$.—The first action of chlorine upon caffeine consists in the production of the chlorocaffeine.

1 equiv. of hydrogen is removed from the caffeine, and an equivalent of chlorine takes its place. This substance is easily obtained pure; the crude chlorocaffeine procured in the manner above described is dissolved in boiling water, filtered, when the solution on cooling deposits the substance as a light bulky mass; after three or four recrystallizations, it is pure. From alcohol it separates in small needles. Admitting for caffeine the formula $C^2\,NH + C^2\,H^5\,N + (C^8\,N^2\,O^4, C^4\,H^4)$, then the formula of chlorocaffeine is $C^2\,NCl + C^2\,H^5\,N + (C^8\,N^2\,O^4, C^4\,H^4)$. When, by the further-continued action of the chlorine, the group $(C^8\,N^2\,O^4, C^4\,H^4)$ is oxidized, the chloride of cyanogen is separated from it, and the methylamine $C^2\,H^5\,N$ combines with the muriatic acid which is formed by the chlorine decomposing water.

Amalic Acid.—The group $(C^8\,N^2\,O^4, C^4\,H^4)$, which is combined in caffeine with $C^2\,NH$ and $C^2\,H^5\,N$, is the combination of the urylic acid $C^8\,N^2\,O^4$, which is contained as conjunct in uric acid with $C^2\,N^2\,H^2$ (*i. e.* urea -2 equivs. water, or the amide of cyanic acid) with the elements of 2 equivs. elayle $(C^2\,H^2)$. The author calls this hypothetical body bielurylic acid.

As in the treatment of uric acid with oxidizing substances urylic acid assimilates oxygen and water, passing into alloxantine, in the same manner the bielurylic acid of caffeine takes up oxygen and the elements of water, and is converted into amalic acid. In the oxidation of uric acid, urea is formed from $C^2\,N^2\,H^2$ by the assimilation of water; in the oxidation of caffeine another base is produced, methylamine. It is evident from the composition of amalic acid, that the alloxantine of Liebig and Wöhler contains 2 equivs. water in combination; its formula therefore is $C^8\,H^3\,N^2\,O^8 + 2HO$, and is produced from urylic acid, $C^8\,N^2\,O^4$, by the absorption of 1 equiv. oxygen and 3 equivs. water, $C^8\,N^2\,O^4 + 3HO + O = C^8\,H^3\,N^2\,O^8$. The $C^8\,H^3\,N^2\,O^8$ furnishes with 2 equivs. water crystallized alloxantine. Bielurylic acid likewise assimilates 1 equiv. oxygen and 3 equivs. water, and is converted into amalic acid, $C^8\,N^2\,O^4, C^4\,H^4 + 3HO + O = C^8\,N^2\,H^3\,O^8$, $C^4\,H^4 = C^{12}\,H^7\,N^2\,O^3$, or alloxane $+2$ equivs. of elayle.

If the formula of alloxantine is $C^8\,N^2\,H^3\,O^8$, then the formation of alloxane consists merely in the assimilation of 1 equiv. oxygen, $C^8\,N^2\,H^3\,O^8 + O = C^8\,N^2\,H^3\,O^9$, which forms with 1 equiv. water crystallized alloxane $= C^8\,N^2\,H^3\,O^9 + HO$. The deportment of amalic acid towards reagents is exactly like that of alloxantine; thereby proving that alloxantine is really contained as such in amalic acid, and that the connexion explained above does in fact exist.

Murexoine, $C^{36}\,H^{23}\,N^{10}\,O^{15}$.—When amalic acid is moistened with a very little water, spread out on a shallow dish and exposed to the air and the vapour of ammonia, it immediately turns rose-red, then violet, and lastly brownish red like peroxide of iron. This mass is pressed between blotting-paper, and exposed to the air until it no longer smells of ammonia; it is dissolved either in warm spirit or in water at 194° F. On cooling, vermilion-coloured crystals of murexoine separate from the solution. These crystals are four-sided

prisms; two of the faces reflect the light with a golden-yellow colour. Under the polishing steel murexoine acquires a metallic lustre and a golden colour. The solution in water cannot be distinguished from a solution of murexide. The solution is not rendered blue by solution of potash, like that of murexide, but decolorized. It is dried *in vacuo*, and then at 212°; it is partially volatilized undecomposed in the form of violet vapours, which condense in the colder portion of the vessel; it must therefore be mixed for combustion cold, as it begins to volatilize at a tolerably low temperature; hence arises the excess of hydrogen in the analyses of this substance. Murexoine, both that dried *in vacuo* and that dried at 212°, that crystallized from alcohol, and likewise that from water, were analysed; no difference was perceptible in the composition. Analysis:—

Carbon.....	43·30	36	= 2700·0	43·29
Hydrogen	5·09	23	287·5	4·61
Nitrogen	27·50	10	1750·0	28·05
Oxygen	24·11	15	1500·0	24·05

The formula $C^{36}\,H^{23}\,N^{10}\,O^{15}=3(C^4\,H^4)+C^{24}\,H^{11}\,N^{10}\,O^{15}$; but the formula $C^{24}\,H^{11}\,N^{10}\,O^{15}$ is that of murexide from uric acid, according to Liebig and Wöhler, less 1 equiv. water. $C^{24}\,H^{11}\,N^{10}\,O^{15}+HO$ is murexide, $C^{24}\,H^{11}\,N^{10}\,O^{15}$, $C^{12}\,H^{12}$ is murexoine.

Just as murexide is formed from 3 equivs. alloxantine, murexoine is produced from 3 equivs. amalic acid.

The brilliant-coloured solutions of murexoine lose their colour on evaporation; when mixed with an acid, they then deposit yellowish crystals, probably the murexane of this series.

Scarcely more than $1\frac{1}{2}$ grm. of pure murexoine is obtained from 4 oz. of caffeine.

Cholestrophane.—The further the action of the chlorine has gone, the less amalic acid and the more cholestrophane is obtained. The latter may also be prepared directly by the oxidation of the amalic acid. The crude cholestrophane is purified by solution in alcohol, and allowing the hot solution to cool slowly. When rapidly cooled, small iridescent spangles are obtained; whilst on slow cooling, colourless transparent plates, an inch and more in length and breadth, and possessing a silvery lustre, are deposited. This substance volatilizes at 212° in vapours, which are deposited upon cold substances in the form of iridescent crystalline plates. Analysis:—

Carbon	42·00	10	42·25
Hydrogen	4·25	6	4·22
Nitrogen.....	20·00	2	19·71
Oxygen	33·75	6	33·82

When 1 equiv. oxygen unites with 1 equiv. amalic acid and 1 equiv. of formic acid is eliminated, cholestrophane is produced—$C^{12}\,H^7\,N^2\,O^8$ amalic acid $+O-C^2\,HO^3$ formic acid $=C^{10}\,H^6\,N^2\,O^6$ cholestrophane.

Cholestrophane stands in the same relation to amalic acid as para-

banic acid to alloxantine; it is parabanic acid + 2 equivs. elayle $C^{10}H^6N^2O^6 = C^4H^4 + C^6H^2N^2O^6$ parabanic acid.

To prove this connexion by experiment, cholestrophane was boiled with solution of caustic potash. The cholestrophane disappears with evolution of an ammoniacal odour; the solution of potash contains much carbonic acid, and gives, on being mixed with a slight excess of nitric acid and solution of nitrate of silver, a white precipitate of oxalate of silver. On boiling cholestrophane in a retort with solution of soda, the sparingly soluble oxalate of soda separated; the vapours condensed in muriatic acid were ascertained to be ammonia by treatment with solution of chloride of platinum, evaporation on the water-bath, washing with a mixture of alcohol and æther, and analysis of the platinum double salt. In what form the C^4H^4 is eliminated in this decomposition could not be ascertained.

This is the same decomposition as parabanic and oxaluric acids experience. If we arrange the products described under each other on one side, and on the other the corresponding products of decomposition of uric acid, we have the following two series:—

Urylic acid.	Bielurylic acid.
$C^8N^2O^4$	$C^8N^2O^4, C^4H^4 = C^{12}N^2H^4O^4$
Alloxantine.	Amalic acid.
$C^8N^2H^3O^8 + 2HO = C^8N^2H^5O^{10}$	$C^8N^2H^3O^8, C^4H^4 = C^{12}N^2H^7O^8$
Parabanic acid.	Cholestrophane.
$C^6N^2O^4 + 2HO = C^6N^2H^2O^6$	$C^6N^2O^4, C^4H^4 + 2HO = C^{10}N^2H^6O^6$
Murexide.	Murexoine.
$C^{24}H^{11}N^{10}O^{15} + HO = C^{24}H^{12}N^{10}O^{16}$	$C^{24}H^{11}N^{10}O^{15}, C^{12}H^{12} = C^{36}H^{23}N^{10}O^{15}$

The members of these two series differ by 2 equivs. of elayle. Probably several such series exist; theobromine may perhaps by oxidation furnish the series which comes in between that of uric acid and caffeine. When treated with chlorine, theobromine yields methylamine. Deducting from the formula of theobromine $C^{14}H^8N^4O^4$, 1 equiv. methylamine and 1 equiv. hydrocyanogen, there remains $C^{10}H^2N^2O^4$, or $C^8N^2O^4, C^2H^2$, which would be elurylic acid, the starting-point of this series.

Just as there are series of alcohols which differ from each other by $n(C^2H^2)$, and the derived series of æthers, aldehydes and fatty acids, so in the present instance we have evidence of the existence of similar series of urylic acids, alloxantines, parabanic acids, murexides, &c.

The product which is formed in the treatment of caffeine with chlorine, and remains in the mother-liquor of the amalic acid and the cholestrophane in the form of a muriatic salt, is methylamine, as formerly suspected by the author. When the mother-liquor is mixed with alcohol, and an alcoholic solution of chloride of platinum added, a pale yellow amorphous precipitate forms in abundance; it is washed with anhydrous alcohol, then dissolved in boiling water; on slow cooling, a beautiful yellow platinum double salt separates in shining plates. Analysis:—

Carbon	4·98	2	5·07
Hydrogen	2·50	6	2·53
Nitrogen	..	1	5·91
Chlorine	..	3	44·91
Platinum	41·46	1	41·58

$$C^2\,H^6\,NCl^3\,Pt = C^2\,H^5\,N,\,ClH + PtCl^2.$$

When this salt is mixed with solution of potash or milk of lime and heated in a retort, methylamine passes over with some aqueous vapour. It may be received in water, or in muriatic acid, or in water containing sulphuric acid; it has a striking resemblance to ammonia.

Methylamine, which is contained in caffeine and theobromine, connects these substances with the oil of Gaultheria, which contains salicylic acid in combination with the oxide of methyle, whilst in the above bases its amide occurs.—*Proc. Royal Acad. Vienna*, July 1850, p. 1–8.

On the Cyanic Amidides. By Messrs. L. Cloez *and* Cannizzaro.

On bringing gaseous chloride of cyanogen and ammoniacal gas into the presence of each other, M. Bineau obtained a solid compound, to which he gave the name of chlorocyanate of ammonia, representing its composition by the formula $CyCl, 2(NH^3)$.

On attempting to form with the new bases of M. Wurtz and the chloride of cyanogen the compounds corresponding to those of ammonia, the results obtained were such as to lead us to re-examine the compounds described by M. Bineau; and we soon became convinced that the chlorocyanate of ammonia was a mixture of the hydrochlorate of ammonia and a species of amide, which we have isolated, and the composition of which may be represented, according to our analyses, by one of the equivalent formulæ—

$$Cy, NH^2, \qquad N(H^2\,Cy), \qquad C^2\,H^2\,N^2.$$

We have named this substance *cyanamide*; the following equation will exhibit its formation:—

$$CyCl + 2NH^3 = NH^3, HCl + Cy, NH^2.$$

The best method of preparing cyanamide consists in passing a current of perfectly dry chloride of cyanogen through a solution of ammoniacal gas in anhydrous æther. Hydrochlorate of ammonia is deposited, which is separated by filtration; and on distilling the ætherial solution in a water-bath, the residue consists of perfectly pure cyanamide.

Cyanamide is a white crystallizable substance, which melts at 104° F., but remains in the liquid state at a far lower temperature. We retained a certain quantity of this substance in the liquid state for twenty-four hours, in a room where the temperature was not above 54°; but on touching the substance with the drawn-out extremity of a pipette, it instantly became solid. At about 302°,

cyanamide exhibits a very remarkable phænomenon; it suddenly solidifies, with disengagement of a large quantity of heat. The composition of the substance thus produced is the same as that of cyanamide, but its properties are different; it has all the characters of *melamine*, which ought, according to this new mode of origin, to be regarded as the amide of cyanuric acid, and called *cyanuramide* or *cyanuramine*, admitting that it results from the tripling of the molecule of cyanamide. Cyanamide does not alter in dry air; it dissolves readily in water; but on evaporating the solution, a residue is obtained, which is nearly insoluble in water, and which we suppose to be cyanuramine. Anhydrous alcohol and æther dissolve it without altering it; alkalies decompose it. It furnishes with some acids, nitric acid* among others, crystalline compounds, which we intend examining.

The volatile bases of M. Wurtz and a arge number of organic alkalies behave in the same manner as ammonia towards the chloride of cyanogen; in general a hydrochlorate of the base and a corresponding cyanic amide are produced. We have already obtained several of these compounds, but as yet have examined only those which result from the action of chloride of cyanogen on methylia, æthylia and amylia, viz. *cyanomethylamide*, *cyanethylamide* and *cyanamylamide*. All these bodies are members of the series of which cyanamide is the first term, as the following table will show:—

Cyanamide ..... $Cy, NH^2 = \left(\begin{matrix}H^2\\Cy\end{matrix}\right)N=C^2\ H^2\ N^2$

Cyanomethylamide $Cy, C^2\ H^4\ N= C^2\left(\begin{matrix}H^4\\Cy\end{matrix}\right)N=C^4\ H^4\ N^2$

Cyanethylamide .. $Cy, C^4\ H^6\ N= C^4\left(\begin{matrix}H^6\\Cy\end{matrix}\right)N=C^6\ H^6\ N^2$

Cyanamylamide .. $Cy, C^{10}\ H^{12}\ N=C^{10}\left(\begin{matrix}H^{12}\\Cy\end{matrix}\right)N=C^{12}\ H^{12}\ N^2$

In certain cases, the chloride of cyanogen, in acting upon a base, may give rise to a new alkali, as observed by M. Hofmann in regard to aniline. The constitution of the bases thus obtained may be represented by the cyanamide of the base acted upon conjoined with the base itself. On this view, the melaniline of M. Hofmann might be represented by the formula—

$$\underset{\text{Aniline.}}{C^{12}\ H^7\ N,}\quad \underset{\text{Cyanilide.}}{C^{12}\left(\begin{matrix}H^6\\Cy\end{matrix}\right)N}\quad =\underset{\text{Melaniline.}}{C^{26}\ H^{13}\ N^3.}$$

The bromide and the iodide of cyanogen produce with ammonia and the volatile alkalies mixtures of the hydrobromate or hydriodate of the alkali acted upon and the corresponding cyanic amide.—*Comptes Rendus*, Jan. 13, 1851.

* Nitric acid, added in small quantity to an ætherial solution of cyanamide, produces nitrate of urea.

On Aloine, the Cathartic Principle of Aloes.

By Messrs. T. and H. Smith.

During last summer, having occasion to prepare a quantity of the aqueous extract of aloes, a preparation in repute with many medical men, we made use of cold rather than hot water as the solvent, from an impression that a more perfect, though less bulky product would be obtained by leaving in the marc a large proportion of resinous matter, which must necessarily be contained in the extract prepared from a hot solution. Further, with a view of rendering the preparation as perfect as possible, the filtered liquid was evaporated *in vacuo*, thereby avoiding an excess of heat, under the influence of which and exposure to the air, recent researches show the cathartic property of the aloes to be seriously impaired.

After the syrupy liquid had cooled, certain appearances arrested our attention, and seemed of sufficient importance to induce a departure from the original intention of forming it into a dry extract. The vessel containing the thin extract was now therefore set aside for a few days; and when again examined, the contents were found to have lost their original liquid state, and to have become loaded with a mass of granular crystalline matter. The whole was at once put into a cloth, and freed from the liquid portion by strong pressure. The crude solid substance left in the cloth being very impure, required further treatment before an opinion as to its nature could be formed, and was therefore dissolved in hot water, and filtered while still hot, out of contact with the air. On the cooling of the liquid, the substance separated in a crystalline state and of a deep yellow colour. After a second pressure, it was subjected to another treatment exactly like the last. The solid cake resulting from the third pressure, after being completely dried, presented the appearance of an opake straw-yellow mass, breaking short and of a dull fracture. Its taste was intensely bitter and distinctly aloetic, but entirely without smell. It was found to be quite combustible, and to leave no ash on being burned on platinum foil. Its solution acted on test-paper neither as an acid nor an alkali; it was therefore a neutral body. It dissolved in very small quantity in cold water, not above a grain to the ounce, but very readily when heated. It is very soluble in acetic æther, and also in acetic acid, of about 25 per cent., even in the cold; 4 grs. may be easily dissolved in a fluid drachm of either of these liquids. In lime-water it is considerably more soluble than it is in cold distilled water. Oil of turpentine and chloroform do not appear to have any solvent action on it. It is very readily dissolved by aqua potassæ and other alkaline liquids. In rectified spirit, with the assistance of heat, it dissolves in large quantity; and on very slowly cooling, out of contact with the air, it crystallizes in beautiful yellow satiny tufts of rhombic plates. The spirituous solution however refuses to give crystals unless above 40 grs. to the fluid ounce of spirit be used. It is therefore very soluble in this menstruum, 12 parts by measure being capable of holding 1 part in solution. Weak spirit is also a good solvent, for

on adding water to a strong alcoholic tincture, there is no separation. Sulphuric æther dissolves it very sparingly.

From a consideration of all these characters, we became satisfied that the substance which had been separated by us from the commercial Barbadoes aloes had never been made known before, and therefore was a new substance; but whether the interest attached to it should terminate here remained to be seen. Of course the first and most important question which suggested itself to the mind, and which remained to be solved, was,—Whether the crystalline substance, which we had now convinced ourselves was an educt, and not a product, from the aloes, possessed any of the virtues of aloes as a medicine, or whether the virtues of aloes were concentrated in it, and depended on its presence for their action upon the living body.

The first trial, with the view of ascertaining its action on the body, was made with ½ a grain, and it acted twelve hours after being taken, in the manner that so characteristically distinguishes the action of aloes. The same quantity was again given to two healthy young men, with a similar result, except that in one about twenty-four hours elapsed before its operation. In the next two cases, 1 gr. failed to act; but in one of these, the dose having been increased to 2 grs., a very strong operation was the consequence. In a case where 4 grs. were given, the person, a patient of Dr. Robertson, Physician to the Edinburgh Royal Infirmary, had been taking ¼ gr. doses of elaterium with little effect. The operation in this case was rather violent. In numerous other cases in which it was tried, it invariably operated in doses of from 1 to 2 grs. The result of these trials was the removal from our minds of every doubt of the crystalline body yielded by the aloes being that on which the cathartic action depended, being in fact the active principle of the drug.

To the new crystalline substance we have given the name of aloine. It was obtained, as already stated, from Barbadoes aloes; and it became a question, both interesting and important, to ascertain whether it could be procured from other kinds, such as the Socotrine and Cape. With this view we therefore put these two kinds of aloes under treatment, operating in the very same way as with the Barbadoes, but without success. That the aloine is present in both of these sorts there cannot be a doubt*. In fact, we have no hesitation in stating our belief, that we shall yet obtain it from these, the result of what little we have done convincing us of its existence in them as well as in the Barbadoes sort; but by the presence of impurities, chiefly we suspect of a resinous nature, the aloine is probably so entangled that it cannot get freedom for that arrangement which seems necessary for ready crystallization. That a crystalline body may be present, and yet may not crystallize, will, we believe, be readily admitted by any one much occupied with the

* Since writing the above, a vessel containing a solution from the Cape aloes, and which had been put aside and remained undisturbed for a long period, has been examined, and found to contain a mass of crystalline matter, exactly of the same appearance as that first obtained from similar solutions of the Barbadoes aloes, which, we feel satisfied, will turn out to be aloine.

process of crystallization. Another cause may perhaps be found in changes and decomposition, originating in faulty processes of preparation, the result of ignorance, carelessness or fraud. That faulty methods of preparing the aloes may be one cause of certain kinds of the drug not yielding aloine, is rendered probable by the following circumstance which came under our observation. If aloine be crystallized, either from water or rectified spirit, and the crystals left in contact with the mother-liquid, in the course of a few weeks, but more quickly in the latter than in the former case, the crystals will have then entirely disappeared, thus showing the readiness with which the aloine loses its crystallizable character. Keeping these considerations in view, and taking advantage of what little we now knew of the properties of the aloine, the following steps were taken:—

The watery solution of Cape aloes having been mixed with a very little sulphuric acid, to separate a quantity of colouring matter along with a fatty acid and chlorophylle, was filtered, and then evaporated *in vacuo* to a thin extract. The extract was shaken with a quantity of æther, which was then poured off, and allowed to evaporate very slowly. Aloine at length crystallized, but of course, from its slight solubility in æther, the quantity was very small; but the thick liquid, which had been washed with the æther, after standing undisturbed for a week or two, was found to have yielded a crystalline crop of aloine considerably more abundant.

The nature of the process by which the presence of aloine in the Socotrine aloes was tested by us was somewhat different from the preceding. A strong alcoholic tincture of the aloes having been prepared, sulphuric æther was added as long as any precipitate was produced. A dark-coloured compound of lime being thus taken out of the way, the æthero-spirituous solution, after becoming quite clear, was mixed with a small quantity of water. The result was a separation of the mixed liquids into two distinct portions; the one heavier, composed of most of the water and spirit and a little æther, forming the under portion; and the lighter, consisting principally of æther, but containing a little spirit and water, floating above it. The heavy liquid having been separated, was exposed to a heat of about 130° F. till the spirit and æther had completely evaporated. The watery solution now left, on cooling gave crystals having the characteristic appearance of aloine, and a trial strengthened this belief of their nature. The lighter liquid, on slow evaporation, likewise produced similar crystals.

The solutions of aloine are wonderfully altered by the action of the air. One striking experiment made by us will perhaps place this character of aloine in as strong a light as any that could be stated. 2 grs. of aloine having been dissolved in 2 oz. of distilled water, the solution, which was of a very pale yellow colour, was corked up in a phial that was nearly filled with it, and then set aside in a heat of about 120° F. The colour of the solution gradually passed into a fine red, deepening continually in intensity, till in a few weeks the colour had become so deep as almost entirely to obstruct the passage of light.

It may not also be without some interest to mention here, the singularly striking effect of nitric acid upon the aloine. ½ a drm. of strong commercial nitric acid being put into a test-tube, and 15 grs. of aloine gradually added, great heat and violent action are produced, with the escape of red fumes, and a perfect solution is the result. The syrupy liquid being now added to cold water, a yellow precipitate is formed, which however dissolves on adding more water; and on neutralizing the liquid with aqua potassæ, a liquid of a splendid red colour is produced. The intensity of the colour is so great, that on comparing it with a liquid of equal bulk, and containing the colouring matter of 2 oz. of cochineal, that coloured by the aloine is of a deeper red, and even in the richness of its shade rivals the other. When the liquid is slowly evaporated, tufts of long needle-shaped crystals of chrysammate of potash are produced.

For an account of the chemical characters of aloine, we beg to refer to an article by our friend Dr. Stenhouse, in the 'London, Edinburgh and Dublin Philosophical Magazine' for December last, from a consideration of which it will be quite obvious, that the substance we have obtained from the aloes is quite different from that described by Mr. Edmund Robiquet*.—*Monthly Journal of Medical Science*, Feb. 1841.

On some Chemical Phænomena of Respiration. *By* M. Horn.

M. Horn gives the following results of his examination of the gases expired from the lungs under different circumstances:—

1. The longer the air is retained in the lungs the greater the proportion of carbonic acid it contains. Thus—

	Carbonic acid.	Oxygen.	Nitrogen.
Under ordinary circumstances.....	3·8	16·3	79·19
The breath held during ten seconds..	5·4	14·5	81·1
The breath held during sixteen seconds	7·2	12·4	80·4

When the gases are expired under pressure, *e. g.* through mercury, the proportion of carbonic acid is still larger. The following average variations have been observed by the author at different periods of the day:—

	Carbonic acid.	Oxygen.	Nitrogen.
Morning.....	3·4	16·70	79·85
Afternoon	4·6	18·68	93·34
Evening.....	3·6	16·42	79·92
After midnight	2·2	14·74	66·42

2. The expiration of carbonic acid is at its minimum at nine o'clock in the evening, and between three and four in the morning; the maximum points of the expiration of carbonic acid are from one to two o'clock in the afternoon, from six to eight in the evening, corresponding with the most frequent periods of exacerbation of disease.

* Dr. Stenhouse obtained in his analysis of aloine which had been dried at 212°, 60·72 C, 5·42 H, and 33·86 O, leading to the formula $C^{34}H^{18}O^{14}$; in the hydrated state aloine contains 1 equiv. water.—Ed. *Chem. Gaz.*

3. The expiration of carbonic acid is augmented after taking food.

4. Infants and growing children expire more carbonic acid than aged persons, men more than women, and individuals of a sanguine and bilious more than those of a lymphatic temperament.

5. Moderate exercise, and the temperate use of spirituous beverages, increase the quantity of carbonic acid expired.

6. Drunkenness and narcotism produce the reverse effect.

7. Pain, sedentary occupations, menstruation, inflammation of the lungs, and fevers, induce a diminution of the quantity of carbonic acid expired.

8. Acute exanthemata augment the proportion.

9. Diarrhœa causes a decrease in the expiration of carbonic acid. —*Gazette Médicale*, 1850; as inserted in the *London Medical Gazette*, Feb. 14, 1851.

ANALYTICAL CHEMISTRY.

Examination of the various Methods of analysing Ashes.

In a paper entitled "Fundamental Experiments on the Determination of the Inorganic Constituents of Organic Bodies," M. Strecker has submitted to criticism the methods proposed by Rose and Erdmann for the analyses of ashes. According to Rose, we must distinguish in organic substances between teleoxidic, meroxidic and anoxidic inorganic constituents. Strecker found, in his experiments, that the inorganic constituents could not be extracted by water and acids from the cinder of the charred organic substance, even with artificial mixtures of charcoal and various substances, when they were contained therein in comparatively small quantity; but, on the other hand, they were completely extracted when present in larger quantity. Now this behaviour accords with that ascribed by Rose to anoxidic substances; they contain small quantities of inorganic constituents, whilst the teleoxidic, as for instance urine, bones, &c., contain large quantities. Now the same is the case with the ashes of plants; and Strecker is therefore of opinion, that the reason why the inorganic substances are sometimes entirely removed by water and acids from the charred mass, and at other times only in part, is owing solely to the proportion of the ash to the cinder, and not at all to any peculiar kind of combination of the inorganic substances with the charcoal.

Strecker then draws attention to the circumstance, that we must not suppose, from the presence of alkaline carbonates in the aqueous extract, that they are always derived from salts of inorganic acids with potash, since tribasic phosphate of potash, after calcination with sugar, yields carbonate of potash to water*. Strecker also ob-

* Does not the formation of alkaline carbonate, when organic matter is heated with tribasic alkaline phosphate, show, in opposition to the statement of Liebig and other chemists, that tribasic phosphate cannot exist in the animal fluids? otherwise alkaline carbonate should be contained in the ash, which they found not to be the case.—Ed. *Chem. Gaz.*

served the production of cyanides and sulphurets on following Rose's method, which may give rise to slight errors in the analysis. There is also a loss of chlorine according to Rose's method, a circumstance which has likewise been observed by Rose and Weber.

Strecker has convinced himself by experiment, that on burning the substances in a muffle according to Erdmann's method, any loss of chlorides and phosphorus can be avoided by the addition of some hydrate of baryta to the substances to be incinerated*. The same chemist has detected in the ashes of nitrogenous substances, for instance of the aqueous extract of blood, of bile, &c., the presence of salts of cyanic acid.

Staffel has likewise submitted Rose's method to examination, and has arrived at the same results as Strecker. For this reason, Staffel prefers the method proposed some time previously by Wackenroder, but so modified that the charred mass is always first exhausted with boiling water, after which the charcoal is incinerated. According to this method, the treatment of organic substances is divided into three parts as follows:—

I. The organic substances, dried at 86° F., are carbonized in a crucible, the lid of which is stuck on with starch-paste. The lid has a hole through which the gases escape; these are set light to. The charred mass is converted by pressure into a coarse powder, emptied into a flask, and repeatedly exhausted with boiling water until the liquid, which is generally transparent, leaves no perceptible residue on evaporation. When the extract is very alkaline, a current of carbonic acid is passed through it, after which it is evaporated to dryness in a platinum crucible until the weight of the residue remains constant.

The solution of the weighed residue is acidified with nitric acid. If, on treating the mass with nitric acid, a separation of silica occur, it is collected on a filter and weighed. The liquid filtered from the silica is mixed with solution of silver, and the chlorine determined from the amount of chloride of silver obtained. The liquid filtered from the chloride of silver is freed from the excess of silver by muriatic acid, and then an excess of ammonia added to it; if no separation of phosphate of lime occur, the ammoniacal liquid is mixed with oxalic acid; and if this produce a precipitate of oxalate of lime, it is collected upon a filter, dried and calcined, and so the amount of lime found. The liquid filtered from the oxalate of lime is now mixed with some chloride of barium; the precipitate of oxalate, sulphate and phosphate of baryta collected upon a filter, dried and calcined, then dissolved in dilute nitric acid, when the sulphate of baryta, if any be present, is left behind, and from its amount the quantity of sulphuric acid is calculated. After removal of the sulphate of baryta, a slight excess of ammonia is added to the acid liquid, the whole set aside for some time; and in case any

* On this point Rose observes, "This certainly has many advantages. But the removal of a large quantity of sulphate of baryta, when lime is present, entails so much inconvenience, that the use of a weighed quantity of carbonate of soda is perhaps preferable."—*Ausführl. Handb.*, vol. ii. p. 782.

phosphate of baryta is deposited, it is collected, dried and calcined, and the phosphoric acid calculated according to the formula BaO $+2PO^5$, proposed by Wackenroder. There is still the potash and soda to determine in the liquid filtered from the oxalate, sulphate and phosphate of baryta. The baryta still contained in the liquid is removed with pure carbonate of ammonia, the liquid filtered from the carbonate of baryta evaporated to dryness in a porcelain dish, and the residue heated to a faint red in a platinum crucible. The residue of alkaline chlorides is dissolved in water, and the potash precipitated from the solution with chloride of platinum; the liquid filtered from the potassio-chloride of platinum is then examined for soda. The author however has, like other chemists, found no soda in inland plants.

II. This consists in the examination of the aqueous extract of the ash obtained by incinerating the charred mass after exhaustion with water. The charcoal is reduced to ash in a Hessian crucible having a slanting position, the ashes weighed, exhausted with hot water eight or ten times, when from 250 to 300 grms. of aqueous extract are obtained from 2 to 3 grms. of ash; these are divided into five or six parts. One part is acidified with nitric acid, mixed with solution of silver, and the chlorine determined from the weight of chloride of silver, and then calculated for the whole of the aqueous extract of the ash. A second portion is acidified with nitric acid, and then mixed with an excess of ammonia to obtain the silica; in general but mere traces are separated. A third likewise weighed portion of the extract is mixed with chloride of barium, and the precipitate, if any form, collected, calcined and weighed; then dissolved in dilute nitric acid; and in case any insoluble sulphate of baryta remain, it is collected, and from its weight the amount of sulphuric acid estimated. The liquid filtered from the sulphate of baryta is mixed with an excess of ammonia, then set aside for some time, the separated phosphate of baryta collected on a filter, dried, calcined and weighed, and calculated according to the above formula. The liquid filtered from the mixed barytic precipitates is used for the determination of the potash and soda; it is freed by carbonate and caustic ammonia from baryta and other earths, evaporated to dryness, the ammoniacal salts dissipated, the residue dissolved in water, and the potash determined by chloride of platinum; the filtered liquid is examined for soda. A fourth weighed portion is mixed with oxalate of potash after acidification with nitric acid. When, as is generally the case, lime is present in the extract, the precipitate of oxalate of lime is heated to a faint red, and the lime calculated from the amount of the carbonate. The liquid filtered from the oxalate of lime is mixed with ammonio-phosphate of soda to precipitate the magnesia.

III. This consists in examining the insoluble portion of the charcoal-ash left in II. This insoluble residue is digested with muriatic acid, and evaporated to dryness to remove the silica, again dissolved in warm muriatic acid, the residual sand and silica collected on a filter, the mixture dried, weighed, and the silica separated from the sand by solution in caustic potash.

The filtered acid liquid is divided into two equal parts, the one half employed for the estimation of the potash and soda, the other for the determination of the earths, peroxide of iron and phosphoric acid, according to the following plan. The one half is heated to boiling in a glass flask, mixed with acetate of soda and some acetic acid; the resulting precipitate, consisting of perphosphate of iron and phosphate of alumina, or of the first only, is collected on a filter, dried, calcined and weighed. To separate the peroxide of iron from the alumina, the weighed precipitate is dissolved in muriatic acid, diluted with water, and heated to boiling for some time with the addition of caustic potash. The separated peroxide of iron is collected upon a filter, and calculated for phosphate of iron according to the formula $Fe^2O^3 + PO^5$, proposed by Wackenroder. The alumina is precipitated from the filtered alkaline liquid by acetic acid as phosphate of alumina $= Al^2O^3 + PO^5$, dried, calcined and weighed. In this case we must not omit to examine the mixed precipitate obtained by acetate of soda for the presence of phosphate of lime, as frequently some is found in ashes which contain much phosphate of lime. If this precipitate be again dissolved in dilute muriatic acid, diluted with water, and heated to boiling with the addition of acetate of soda, it is obtained free from every trace of phosphate of lime. After the alumina and peroxide of iron have been precipitated by acetate of soda from the acid extract of the ash in the state of phosphate, the separated liquid is mixed with a solution of perchloride of iron (the amount of iron in which is known, and equal in weight to about the tenth or twentieth part of the entire weight of the ash), in order to determine the phosphoric acid still contained in it; the liquid itself is diluted with a considerable amount of water, heated to boiling in a flask with the addition of 0·5 grm. chlorate of potash, somewhat neutralized with carbonate of soda, and the whole of the iron added to the liquid thrown down as basic phosphate by a further addition of acetate of soda. The precipitate is collected on a filter, washed, dried, and ignited in a platinum dish after having been moistened with a few drops of nitric acid, and in this way a basic phosphate of iron obtained perfectly free from protoxide. The liquid filtered from the basic phosphate of iron is heated to boiling in a flask with carbonate of soda, in order to precipitate lime, magnesia and protoxide of manganese as carbonates. The filtered liquid is mixed with some phosphate of soda and ammonia, and the crystalline precipitate of ammonio-phosphate of magnesia obtained after twelve to twenty-four hours, added to that portion to be mentioned hereafter. The mixed precipitate of earthy carbonates is, after drying, heated to a strong red in a porcelain crucible, then dissolved in cold dilute nitric acid. If any manganese be present, it is left as Mn^3O^4. The separated liquid is mixed with oxalate of potash, the oxalate of lime calcined after drying, and calculated from the amount of carbonate. After separating the oxalate of lime, the liquid is mixed with ammonio-phosphate of soda free from magnesia. The crystalline precipitate obtained in the course of twelve hours' standing is mixed with that previously obtained, calcined, and the weight of magnesia calculated from it.

As the salts of potash cannot be always completely removed from the ashes by water, the second half of the acid solution is separated from all the earths by carbonate and caustic ammonia, the liquid evaporated to dryness, heated to redness to remove the ammoniacal salts, the residue dissolved in water, the potash precipitated by chloride of platinum, and the filtered liquid then tested for soda.—Liebig's *Annalen*, lxxiii. p. 339; and *Archiv der Pharm.*, lxiv. p. 1.

PROCEEDINGS OF SOCIETIES.

Royal Society.

December 12, 1850.

(Sir Frederick Pollock, Lord Chief Baron, V.P., in the Chair.)

"On the Action of Nitric Acid on various Vegetables, with a more particular examination of *Spartium scoparium*, Linn., or Common Broom." By John Stenhouse, Esq., F.R.S.

This paper is a continuation of a series of investigations intended to elucidate the nature of vegetables by means of chemical reagents. A preceding paper contained an account of the effects produced by the action of sulphuric and hydrochloric acids on the *matière incrustante* of several plants belonging to different great classes of vegetables. The effects of nitric acid upon a variety of vegetable groups are now described; the researches having been undertaken in the hope that by means of this powerful reagent some light might perhaps be thrown on peculiarities in their respective constitutions.

The first plant experimented on with this view, was the *Populus balsamifera*, as representing the numerous family of the Poplars. A quantity of the smaller branches of this tree, cut into pieces, was exhausted with boiling water. The dark-coloured bitter-tasted liquid which it yielded was evaporated to the state of an extract, which was digested for nearly twenty-four hours with dilute nitric acid. This strongly acid solution was evaporated to dryness on the water bath, the dried residue was dissolved in a considerable quantity of hot water, and the solution after cooling was carefully filtered. The clear liquid, after concentration to a very moderate bulk, was exactly saturated with carbonate of potash. A yellow crystalline sediment quickly appeared. It consisted of nitropicrate of potash, and the potash salt of a new acid, to which the author has given the name of *nitropopulic acid*. The mixed potash salts were then collected on a filter, dried by pressure, and were treated with a cold solution of dilute carbonate of potash, which readily dissolved out the nitropopulate of potash, while it left the nitropicrate of that base unacted on. The two salts were then separated by filtration, the nitropicrate remaining on the filter, while the nitropopulate was dissolved in the alkaline liquid. The solution was next slightly supersaturated with hydrochloric acid, when the nitropopulate of potash precipitated as a compact crystalline powder, which was purified by repeated crystallizations out of hot water. When pure, the potash

salt, which crystallizes in small lemon-yellow prisms, is boiled with a considerable excess of hydrochloric acid, and, on the cooling of the solution, the nitropopulic acid is deposited in silky needles, forming concentric groups of a pale yellow colour. By digestion with animal charcoal, the nitropopulic acid is rendered perfectly colourless. It is very soluble in water, and still more so in weak and strong spirits of wine. By digestion with strong nitric acid, it is rapidly converted into nitropicric acid. In several of its characters nitropopulic acid bears a considerable resemblance to indigotic acid. When subjected to analysis, the formula of nitropopulic acid dried in the air, was found to be $C^{14}\,H^{3}\,N^{2}\,O^{13}+HO+2Aq$; that of the acid dried at 212° F., $C^{14}\,H^{3}\,N^{2}\,O^{13}+HO$.

The potash, silver, soda and baryta salts were also analysed.

The *Populus nigra*, when treated with nitric acid, was also found to yield nitropopulic acid, which appears therefore to be characteristic of the poplar tribe.

An extract was also prepared from *Salix russelliana*, or the Bedford-willow, which, when it was digested with dilute nitric acid, yielded a great deal of oxalic and nitropicric, but no nitropopulic acid. Extracts of the *Cytisus laburnum*, or the laburnum-tree; of the *Swetenia mahogani*, or the mahogany-tree; of the *Pyrus malus*, or the apple-tree; of the *Cratægus oxyacantha*, or the hawthorn; of the *Ribes nigrum*, or the black currant bush; of the *Betula alnus*, or the alder; of the *Ulex europæus*, or the furze; of the *Calluna vulgaris*, or common heather; of the root of the *Curcuma longa*, or turmeric; of the seeds of the *Bixa orellana*, or annotto; of the *Sambucus nigra*, or the elder; of the *Cytisus scoparius*, the *Spartium scoparium* of Linn., or common broom, when treated with dilute nitric acid, also yielded oxalic and nitropicric acids. The extracts of *Quercus robur*, or common oak, and of *Betula alba*, the birch-tree, when digested with nitric acid, only yielded oxalic acid, but no nitropicric or any analogous nitrogenated acid.

The results of these experiments seem to indicate therefore that a far greater number of plants are capable of yielding nitropicric acid than has generally been supposed, those which fail to do so constituting a very small minority.

As the extract of broom, *Spartium scoparium*, besides yielding nitropicric acid, exhibited some interesting peculiarities, it was subjected to a more minute examination. When an aqueous decoction of broom was concentrated to about a tenth of its bulk, and set aside in a cool situation for twelve hours, it gelatinized into a greenish-brown coherent mass, which was thrown upon a filter and washed with a little cold water. It consisted chiefly of a yellow crystallizable colouring matter (scoparine, the diuretic principle of broom), which was at first contaminated with a considerable amount of chlorophyl. It also contained a small quantity of a volatile organic base (sparteine, the narcotic principle of broom), the greater portion of which however remained in the mother-iquors.

The scoparine, when purified by repeated crystallizations out of

hot water and spirits of wine, formed pale yellow prisms of a feeble acid character. Its formula was found to be C^{21} H^{11} O^{10}. Scoparine acts as a powerful diuretic.

The mother-liquor from the crude scoparine, after having been concentrated to a very moderate bulk, was distilled along with a considerable excess of soda, when a colourless basic oil slowly collected at the bottom of the receiver. This oil was the volatile base sparteine. It has a strongly alkaline reaction, completely neutralizing the most powerful acids. It is but slightly soluble in acids, but readily dissolves both in alcohol and in æther. It boils at about 550° F. The taste of its salts is very bitter. The formula of this base is C^{15} H^{13} N. The nitrate, sulphate and hydrochlorate of sparteine are exceedingly soluble, and crystallize with great difficulty. The nitropicrate of sparteine forms long, slender brittle needles, undistinguishable from nitropicrate of potash. Its formula is C^{15} H^{13} N, HO, C^{12} H^2 N^3 O^{13}.

The double chloride of platinum and sparteine crystallizes in rectangular prisms. This salt contains two equivalents of water, which it loses at 266° F. Its formula, when dried at 212° F., is C^{15} H^{13} N, HCl + Pt Cl^2 + 2HO.

The double mercurial salt crystallizes in large, right rhombic prisms, exhibiting the diamond lustre. Its formula is C^{15} H^{13} N, HCl, Hg Cl.

Sparteine appears to be a strong narcotic poison, though much inferior in this respect to either nicotine or coneine.

It is plain, therefore, that in employing a decoction of broom-tops in dropsical affections, as has hitherto been the practice, the patient is subjected to the narcotic influence of the sparteine, as well as to the diuretic effects of the scoparine, a result which in general is not likely to be desirable. The author does not, however, think it is at all necessary to employ chemically pure scoparine for medical purposes. If a decoction of broom be evaporated to dryness on the water-bath, then treated with a little dilute hydrochloric acid, the mixture thrown upon a filter and washed with a small quantity of cold water, almost the whole of the sparteine will be removed, and the dark green gelatinous mass remaining on the filter will be found to possess the diuretic without the narcotic properties of the plant.

February 13, 1851.

(Sir Benjamin C. Brodie, Bart., V.P., in the Chair.)

"On Rubian and its Products of Decomposition." By Edward Schunck, Esq., F.R.S.

After pointing to the obscurity in which the inquiry concerning the state in which the colouring matter of madder originally exists in this root is involved, the author refers to the change which takes place in the root, especially if in a state of powder, during the lapse of time, and to the little light which has been thrown by chemical investigations on the nature of the process by which the change is effected. He states that it has been suspected by several chemists that there exists originally some substance in madder, which, by

the action of fermentation, or oxidation, is decomposed, and gives rise by its decomposition to the various substances endowed either with a red or yellow colour, which have been discovered during the chemical investigations of this root. In his papers on the colouring matter of madder, he has described four substances derived from madder, only one of which is a true colouring matter, but all of them capable under certain circumstances, as for instance in combination with alkalies, of developing red or purple colours of various intensity. After referring to the opinions of M. Persoz and the investigations of Mr. Higgin* relative to xanthine and alizarine, the author observes that, by adding a variety of substances to an extract of madder with cold water, he was enabled to ascertain under what circumstances and by what means the tinctorial power of the liquid is destroyed, and consequently what is the general character of the substance or substances to which it is due. He found that by adding sulphuric or muriatic acid to the extract, and heating, the liquid after neutralization of the acid was no longer capable of dyeing. The tinctorial power was also destroyed by the addition of hydrate of alumina, magnesia, protoxide of tin, and various metallic oxides, but not by carbonate of lime or carbonate of lead. In all cases in which the property of dyeing in the extract was destroyed, he invariably found that its bitter taste and bright yellow colour were destroyed. Having shown, in his former papers on this subject, that the intensely bitter taste of madder and its extracts is due to a peculiar substance to which he has given the name of *rubian*; and as it appeared from these preliminary experiments that this substance, though itself no colouring matter, is in some way concerned in the changes whereby a formation of colouring matter is induced in aqueous extracts of madder, he proposed to himself to examine its properties and products of decomposition more in detail than he had hitherto done.

After numerous experiments, undertaken with the view of obtaining pure rubian in quantities sufficiently large for the purposes of examination, he discovered a property of that substance, namely the remarkable attraction manifested by it towards all substances of a porous or finely-divided nature, which is perhaps more characteristic of it than any other, and by which he was enabled to obtain it in a state of purity. The method he finally adopted, and which, he states, surpasses all others in facility and certainty of execution, is fully detailed.

Rubian, when prepared according to this method, is a hard, dry, brittle, shining, perfectly uncrystalline substance, similar to gum or dried varnish. It is not in the least deliquescent, as xanthine is described to be. In thin layers it is perfectly transparent, and of a beautiful dark yellow colour; in large masses it appears dark brown. It is very soluble in water and in alcohol, more so in the former than in the latter; but insoluble in æther, which precipitates it in brown drops from its alcoholic solution. Its solutions have an intensely bitter taste. When it is pure, its solution in water gives no

* Phil. Mag., xxxiii. p. 282.

precipitates with the mineral or organic acids, nor with salts of the alkalies or alkaline earths. Basic acetate of lead however gives a copious light red precipitate in a solution of pure rubian, the solution becoming colourless; but this is the only definite compound of rubian with which the author is acquainted. He states that rubian cannot be considered as a colouring matter in the ordinary sense of the word. It is decomposed by acids, alkalies, chlorine, heat and ferments. The formula for rubian appears to be $C^{56} H^{34} O^{30}$.

The action of sulphuric and of muriatic acid on rubian is stated to be precisely the same. The products of the decomposition by those acids are,—1st, *alizarine*; 2nd, the substance which he formerly termed β-resin, but which he now calls *verantine*; 3rd, the substance which the author in former papers has called α-resin, but to which he now prefers giving the name of *rubiretine*; 4th, a body which has not hitherto been observed, and which he denominates *rubianine*; and 5th, a sugar obtained from the acid liquid after the complete decomposition of the rubian.

1. The alizarine obtained from the decomposition of rubian exhibits all the usual properties of this well-known substance. Its colour is dark yellow, without any tinge of brown or red. The crystals possess a lustre which the author has never seen equalled in this substance. The analysis gave the formula $C^{14} H^5 O^4$. By simply losing 14 equivs. of water, 1 equiv. of rubian is converted into 4 equivs. of alizarine.

2. Verantine, in most of its properties, coincides with the substance to which the author formerly gave the name of β-resin of madder. When prepared according to the method described in the paper, it is obtained in the form of a reddish-brown powder. When heated on platinum foil, it melts, and then burns away without leaving any residue. It dissolves in concentrated sulphuric acid with a brown colour, and is reprecipitated by water in brown flocks. On heating the solution in concentrated sulphuric acid, it becomes black, sulphurous acid is disengaged, and the substance is decomposed. Concentrated nitric acid dissolves it on boiling, with a disengagement of nitrous acid, forming a yellow liquid, from which nothing separates on cooling. It is almost insoluble in boiling water, but readily soluble in boiling alcohol, and is again deposited on the alcohol cooling as a brown powder, which is its most characteristic property.

From an experiment described in the paper, the author is inclined to conclude that alizarine and verantine are capable of forming a double compound with alumina soluble in boiling water, and that a mixture of the two in the proportion in which they exist in this compound constitutes what has been called purpurine.

Although the difficulty of obtaining pure verantine in sufficient quantity for the purposes of analysis prevented the author from determining its composition with the requisite accuracy, he obtained approximations sufficiently near to remove almost all doubts on the question. The formula deduced from four experiments is $C^{14} H^5 O^5$; so that it appears that verantine differs from alizarine by containing 1 equiv. more of oxygen.

3. Rubiretine is identical with the substance which the author

formerly called α-resin of madder. He endeavoured in vain to determine the atomic weight of this substance; but states that there is only one formula which is in accordance with his analyses, and at the same time satisfactorily explains its formation. This formula is $C^{14} H^6 O^4$, so that 2 equivs. of verantine and 2 equivs. of rubiretine with 12 equivs. of water give 1 equiv. of rubian.

4. Rubianine greatly resembles rubiacine in its appearance and many of its properties. It may however easily be distinguished by several characteristics, and above all by its composition. It is obtained from a solution in boiling alcohol in the form of bright lemon-yellow silky needles, which when dry form an interwoven mass. It is less soluble in alcohol, but more so in boiling water, than any of the preceding substances. On the solution in boiling water cooling, it crystallizes out again in yellow silky needles. Its colour is lighter than that of rubiacine. When heated on platinum foil, it melts to a brown liquid; then burns, leaving a carbonaceous residue, which on further heating disappears entirely. It is soluble in concentrated sulphuric acid, with a yellow colour; the solution on boiling becomes black, and gives off sulphurous acid. It is not affected either by dilute or concentrated nitric acid even on boiling; it merely dissolves in them, and on the acid cooling, crystallizes out again as from boiling water.

There are three formulæ, all of which give for 100 parts of this substance numbers not widely differing from those deduced from the analyses, viz. $C^{28} H^{17} O^{13}$, $C^{32} H^{19} O^{15}$, $C^{44} H^{24} O^{20}$, but the last is that with which they best agree.

5. The sugar is always obtained in the form of a transparent yellow syrup, which neither crystallizes, however long its solution may be left to stand, nor becomes dry unless heated to 100° C. There are two formulæ, $C^{14} H^{14} O^{14}$ and $C^{12} H^{12} O^{12}$, both of which agree with the analyses of this substance, and explain its formation. The author states the views to which each of these formulæ gives rise, and the reasons for adopting the latter.

Although five substances are produced by the action of acids on rubian, the author does not consider that these substances are all formed together, or in other words, that 1 atom of rubian, by its decomposition, gives rise to all five at the same time; but that, from the composition of these substances as compared with that of rubian, it follows, that the decomposition affects three separate atoms of rubian. One of these atoms loses 14 atoms of water, and is converted into alizarine. The second loses 12 atoms of water, and then splits up into verantine and rubiretine. The third takes up the elements of water, and then splits up into rubianine and sugar. Whether it would be possible to confine the decomposition of rubian entirely to one of these processes, or whether all three are essential, he considers is a question of the highest importance, not so much in a theoretical as in a practical point of view; and that should any chemist succeed in changing rubian entirely into alizarine, he would be the means of giving a great stimulus to many branches of manufacture and adding largely to the national wealth.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Root of Chiococca racemosa.

By Prof. Rochleder *and* Dr. Hlasiwetz.

François, Pelletier and Caventou discovered in the root of *Chiococca racemosa* a peculiar bitter substance, called *caincine* or *caincic acid*, which was analysed by Liebig, who advanced for it the formula $C^8 H^7 O^4$. Brandes found in this root a basic substance which he called *chiococcine*, but which Von Santen declared to be identical with emetine.

The authors have recently submitted this root to further examination; few soluble substances occur in the wood; by far the larger proportion is contained in the bark of the root. By crushing the root dried at 212°, the bark separates from the wood, and can in this manner be very nearly isolated.

The bark contains caffeotannic acid, of which an extremely small quantity is contained in the wood. The bark likewise contains caincic acid. When the bark of the root is exhausted with boiling alcohol, and the filtered liquid mixed with a spirituous solution of acetate of lead, a yellow precipitate falls, consisting of caffeotannate of lead; it likewise contains some caincate of lead and the lead salts of inorganic acids, especially phosphoric acid. The liquid filtered from this precipitate furnishes with tribasic acetate of lead a very pale yellow precipitate, consisting principally of caincate of lead contaminated with a small quantity of caffeotannate of lead. Easy as it is to separate the greater portion of the caincic acid from most of the caffeotannic acid, it is exceedingly difficult to remove the last traces of caincic acid from the caffeotannic acid, and to obtain caffeotannic acid, or one of its salts, in a state of purity.

Caffeotannic Acid, $C^{28} H^{17} O^{15}$.—By decomposing the first precipitate above mentioned with sulphuretted hydrogen, and partial precipitation of the liquid thus obtained by a solution of neutral acetate of lead, and a frequent repetition of this process, the author succeeded in obtaining a lead compound of caffeotannic acid perfectly free from caincic acid. The acid separated from this salt possessed all the properties of that contained in coffee beans; it strikes a dark green colour with persalts of iron, furnishes yellow compounds with oxide of lead, turns green when mixed with ammonia and exposed to the air; the green solution becomes brown on the addition of acetic acid, and then gives a blue precipitate with

acetate of lead. Mixed with potash and exposed to the air, it turns brown. In the analysis this acid gave 25·66 per cent. oxide of lead; and for the organic substance in combination with it, after deducting the oxide of lead,—

Carbon	54·91	28	55·08
Hydrogen	5·52	17	5·37
Oxygen	39·57	15	39·35

$C^{28}\,H^{17}\,O^{15} = C^{14}\,H^{8}\,O^{7} + C^{14}\,H^{8}\,O^{7}$, HO.

Caincic Acid, $C^{16}\,H^{14}\,O^{8}$, is obtained when the second pale yellow precipitate above mentioned is decomposed with sulphuretted hydrogen, the liquid filtered from the sulphuret of lead somewhat concentrated, and then set aside. After a time a flocculent precipitate forms, which appears under the microscope to consist of a tissue of four-sided prisms. A further quantity of caincic acid is obtained when the first yellow precipitate which a solution of neutral acetate of lead produces in the spirituous decoction of the bark of the root is decomposed with sulphuretted hydrogen, the liquid filtered from the sulphuret of lead; after expelling the excess of sulphuretted hydrogen, precipitated with a solution of neutral acetate of lead, and the liquid filtered from the precipitate thrown down with tribasic acetate of lead. The precipitate is decomposed with sulphuretted hydrogen, and the liquid filtered from the sulphuret of lead concentrated by evaporation on the water-bath, and set aside. After a time the caincic acid crystallizes out. The acid obtained from both precipitates is collected upon a filter, the mother-liquor let drain off, the mass then washed with a little cold water, finally pressed between frequently-renewed sheets of blotting-paper, and dissolved in the smallest quantity of boiling water to which a little alcohol has been added. The filtered solution deposits on cooling the caincic acid, the quantity of which increases somewhat on standing. It is obtained perfectly pure after four or five recrystallizations.

Caincic acid forms a pure, white, silky, inodorous mass, consisting of a tissue of slender needles; is decomposed by heat, with the diffusion of an odour resembling olibanum, and leaves on combustion not a trace of ash. It dissolves in water and alcohol, gives no colour with persalts of iron, and yields pure white precipitates with salts of lead; alkalies produce no change in the solution. Dilute sulphuric, muriatic and nitric acids cause an instantaneous decomposition on warming the aqueous solution; an insoluble substance separates in gelatinous flakes, and another substance remains in solution; the acid entirely disappears. The pure acid, dried at 212°, yielded the following results on analysis:—

C	58·40	58·08	58·34	58·18	58·13	16	1200·0	58·18
H	7·60	7·77	7·93	7·87	7·72	13	162·5	7·88
O	34·00	34·15	33·73	33·95	34·15	7	700·0	33·94

The formula differs from the early one of Liebig's by 1 equiv. of water, $C^{16}\,H^{14}\,O^{8} = C^{16}\,H^{13}\,O^{7} + HO$.

Acid Caincate of Lime, $10(C^{16}H^{13}O^{7})+4CaO+15Aq$.—In the spirituous extract of the bark of the root, a certain amount of lime is contained. The precipitates produced by lead salts consequently contain lime, which passes into the liquid on their decomposition by sulphuretted hydrogen. When such a solution containing lime is evaporated on the water-bath to a syrupy consistence, and mixed with a large quantity of absolute alcohol, a white flocculent substance forms, which is an acid lime-salt of caincic acid; it was washed with alcohol on a filter, pressed between blotting-paper, and dried at 212°:—

Carbon	50·31	50·43	160 =	12000·0	50·61
Hydrogen		7·60	145	1812·5	7·64
Oxygen		36·50	85	8500·0	35·85
Lime	5·69	5·47	4	1400·0	5·90

Lead Salt I. *of Caincic Acid.*—A solution of pure caincic acid and alcohol furnishes with an alcoholic solution of neutral acetate of lead a small quantity of a white precipitate, which had the following composition after being dried at 212°:—

Carbon.....	34·95	16 =	1200·0	34·71
Hydrogen	4·45	13	162·5	4·70
Oxygen	20·30	7	700·0	20·25
Oxide of lead	40·30	1	1394·5	40·34

Lead Salt II.—With tribasic acetate of lead, a copious, white, mucilaginous precipitate is obtained from a solution of caincic acid. It is difficult to wash, and has the following composition:—

Carbon	26·60	48 =	3600·0	26·67
Hydrogen	..	42	525·0	3·89
Oxygen	..	24	2400·0	17·78
Oxide of lead	51·40	5	6972·5	51·66

The analysis of the first lead salt gives somewhat too little hydrogen, and comes nearest to the formula $C^{16}H^{12}O^{7}$. But this formula does not harmonize with the analysis of the pure acid, nor with the products of decomposition.

Chiococcaic Acid.—When caincic acid is dissolved in a solution of caustic potash, some pieces of potash added to the solution, and the mixture heated in a silver dish, the mass froths considerably, turns yellow with evolution of gas, and a yellowish brown mass is obtained, which, when the heat has not gone too far, deposits, after solution in water and the addition of acetic acid, a gelatinous substance, with disengagement of carbonic acid. This gelatine is obtained much easier, and in larger quantity, by treating an aqueous solution of caincic acid with dilute acids. On cooling, the clear liquid becomes turbid, and, if it was concentrated, thick, and deposits, upon the addition of water, a flocculent mass, which is readily soluble in alcohol, but insoluble in water. The authors call this substance *chiococcaic acid.*

To obtain this acid pure, it is dissolved in boiling spirit, from which, if sufficiently weak, the greater part separates on cooling.

The yellowish mother-liquor is absorbed by the separated acid as by a sponge. The mass has great resemblance to a transparent soap. The liquid is separated by pressure between fine linen, the substance again dissolved in spirit, and this process repeated until the alcoholic solution is perfectly colourless. This solution is precipitated by water in a gelatinous form. A solution of acetate of lead produces in it a white precipitate, which, washed with alcohol and dried at 212°, had the following composition :—

Carbon	42·96	192	42·92
Hydrogen.....	5·30	144	5·36
Oxygen.....	14·03	48	14·31
Oxide of lead	37·71	9	37·41

This would lead to the formula $C^{192}H^{144}O^{48},9PbO = 16[C^{12}H^{9}O^{3}] + 9PbO$.

Chiococcaic acid, burnt alone, gave the following results :—

Carbon	70·18	69·78	69·77	48=3600·0	70·07
Hydrogen	8·95	8·65	8·78	35	437·5	8·52
Oxygen	20·87	21·57	21·45	11	1100·0	21·41

leading to the formula $C^{48}H^{35}O^{11} = 4(C^{12}H^{9}O^{3}) - HO$.

A gelatine prepared from pure caincic acid gave, after being dried *in vacuo*,—

Carbon	68·40	12 = 900·0	68·57
Hydrogen	8·83	9	112·5	8·57
Oxygen	22·77	3	300·0	22·86

The acid dried *in vacuo* is white, that dried at 212° has a yellowish-gray tint. In the freshly-precipitated state it resembles a gelatine of silica; it dries to a transparent horny mass, which is easily rubbed to powder. On being heated, it turns black; some shining crystals sublime, amounting to little in weight; and then a very thick oil, having a strong odour of olibanum and naphtha, distils over. The distillate has an acid reaction. Chiococcaic acid contains the elements of oil of turpentine or an isomeric body, and formic acid $C^{12}H^{9}O^{3} = C^{10}H^{8} + C^{2}HO^{3}$; deducting the formula of chiococcaic acid from the formula of caincic acid, there remains that of a carbohydrate, $C^{16}H^{13}O^{7} - C^{12}H^{9}O^{3} = C^{4}H^{4}O^{4}$.

To decide whether $C^{4}H^{4}O^{4}$ was contained in caincic acid in the form of acetic acid, or any similar form, pure crystallized caincic acid was heated with dilute sulphuric acid in a retort. Neither carbonic acid nor a combustible gas is disengaged. The liquid was heated for several hours in a water-bath, filtered from the gelatine, and mixed with baryta water. The precipitate was separated from the liquid, and the excess of baryta in solution was removed as carbonate by passing carbonic acid into the liquid, heating and filtering. The liquid was evaporated to dryness in the water-bath, the residue dissolved in alcohol, separated from a few flakes, and again evaporated on the water-bath to dryness. It left a residue of a sweetish insipid taste and a faint yellowish colour, which diffused, on being heated, a peculiar smell of burnt sugar, and proved, by its behaviour

towards solution of sulphate of copper and potash, to be grape-sugar. Caincic acid is consequently a conjugate compound of chiococcaic acid and a carbohydrate, which latter is separated from the chiococcaic acid, and converted into grape-sugar by the action of acids. This is the reason why caincic acid, on being heated with an excess of hydrate of potash, diffuses the odour of metacetone, which is no longer the case with chiococcaic acid. This constitution would place caincic acid by the side of salicyle, phloridzine and amygdaline, which are likewise conjugate compounds containing a neutral carbohydrate.

Chiococcaic acid stands in the same relation to caincic acid as gallic to tannic acid:—

Caincic acid	$=C^{16}H^{13}O^{7}$	Tannic acid	$=C^{18}H^{5}O^{12}$
Chiococcaic acid	$=C^{12}H^{9}O^{3}$	Gallic acid	$=C^{14}H^{4}O^{8}$
	$C^{4}H^{4}O^{4}$		$C^{4}H^{4}O^{4}$

Proc. Acad. Vienna, 1850.

On an Oxide of Tin found in the Slags of the Copper Furnaces.

By Mr. John Cameron, F.C.S.

In the Number for October 1, 1849, of the 'Chemical Gazette,' there appeared a paper by M. Daubrée "On the Artificial Production of a crystallized Oxide of Tin," by passing the vapour of water and perchloride of tin through a porcelain tube heated to redness. The product, according to the account given in that paper of his experiment, was a crystalline stannic acid, the specific gravity of which he gave as 6·72, and the crystalline form a right rhombic prism. Some time previous to the appearance of the paper in the 'Chemical Gazette,' I had observed a crystalline substance in the slags of the copper furnaces at certain stages of the process, which on examination I found to be a compound of tin; and when I read the account of the artificial production of a crystallized stannic acid, I concluded that they were one and the same, as they were produced under similar circumstances. I collected a quantity of the crystals, and digested them in nitric acid for a considerable time, to free them from adhering oxide of copper; after which I mixed them intimately with a reducing flux consisting of carbonate of soda and black flux, and submitted the mixture to a white heat in the common Cornish crucible, by which means I obtained a button of metallic tin.

Shortly after I had found the crystals to be a compound of tin, the paper of M. Daubrée appeared in the 'Chemical Gazette,' and I believed at the time that they were the same. Recently however I took the specific gravity of the crystals that I observed, and found it by experiment to be by

		Mean.
First experiment	3·04	2·9372
Second experiment.....	2·8345	

From this it would appear that the oxide formed in the copper furnaces is not the same as that described by M. Daubrée, the spe-

cific gravity of which is more than twice the sum of that which I have found. On examination, I found the form of the crystals quadrilateral prismatic, and possessing a vitreous lustre. These crystals are not changed when submitted alone to a white heat, and are perfectly insoluble in nitric, sulphuric and hydrochloric acids, and scarcely anything dissolved by *aqua regia* from them. Heated in a test-tube in contact with phosphorus, potassium and sodium, they are decomposed, and globules of metallic tin deposited in the bottom of the tube. In order to satisfy myself that it was an oxide, I reduced some of the crystals to a very fine powder in an agate mortar, and placed it in a tube open at both ends. To the one end I attached another tube containing chloride of calcium, and to the other end I attached an empty glass tube with a bulb at one end of it. A current of hydrogen was then passed through the chloride of calcium over the powdered crystals, and a spirit-lamp at the same time applied to the tube containing the oxide till it was heated to redness. It soon began to darken in colour, and shortly after globules of tin appeared on the surface of the powder, and a quantity of water was deposited in the bulb of the tube attached. From one analysis which I have made of this compound, it would appear to be a quadroxide of tin, $Sn O^4$; but as the ascertaining its exact composition will require some further research, I reserve that for a future communication.

Spitty Copper Works, Llanelly, March 20.

On the Spheroidal State of Bodies. By E. N. Horsford, *Rumford Professor in Harvard University, Cambridge, America.*

Cambridge, Feb. 18, 1851.

Dear Sir,—I enclose, with a request for publication in your Journal, a short paper recently submitted to the American Academy.

I am, very respectfully, yours,

Dr. Francis. E. N. Horsford.

From the early observations of Leidenfrost and the later extended researches of Boutigny upon the so-called spheroidal state of bodies, much attention has been directed to the interesting phænomena considered under this name, and to the speculation, that a new law, superseding the ordinary laws of heat, was here illustrated.

It will be the object of this communication to show that these phænomena are not rare, and that they require no new law for their explanation.

In the experiment of dropping water upon a hot polished metallic surface, as into a hot platinum crucible, we have three bodies concerned in the phænomenon that follows, viz. the supporting surface, the water, and the layer of vapour interposed between them. The water rests upon a cushion of steam, continuously evolved by heat from the water, and assumes rounded margins as a result of the gravity of its particles toward its own centre. Its condition approxi-

mates to that of a liquid entirely surrounded by a uniformly-elastic medium, as, for example, a drop of molten lead in air, and permits a proportionate approximation to the spherical form.

It is essential only that there be two bodies, one of them being fluid, between which affinity is wanting.

Corresponding with water in the ordinary experiment, called by the name of Leidenfrost, æther, alcohol, turpentine, a great variety of essential oils, and many other liquid bodies, may be employed. The conditions are the same. The liquid evolves a vapour, which, constantly issuing, prevents contact with the supporting surface. Here are three bodies and a high temperature.

Æther and oil dropped on water assume the spheroidal state. They have no affinity for the water. Here but two bodies and no heat are required. Quicksilver poured upon glass assumes the spheroidal state. It has no affinity for the glass. Here but two bodies are concerned. Water dropped upon glass strewn with charcoal dust or fine powder, like pollen, takes on the spheroidal state. Potassium and sodium thrown upon water assume this state. In the decomposition of the water producing potash, hydrogen is evolved; and with the heat arising from this union, and that of the potash with water forming hydrate of potash, water is vaporized, which with the hydrogen keeps the floating sphere and water apart. The dew-drop presents a spheroidal but little differing from the true spheroidic state. It rests in most cases upon the hairs or down with which leaves are covered, and is not in contact with the leaves or twigs.

The bead, as it is called, which appears at the surface of some liquids when violently shaken, and of which we have a familiar example on the water around the prow of an advancing sail-boat, is an instance of the spheroidal state of great interest. What prevents the prompt reunion of the bead with the mass is not so obvious.

There is a fact in the history of the barometer which merits attention, and which may have influence in explaining this phænomenon. When pure mercury has been introduced into a barometric tube, and thereafter boiled, so as to expel all the air, upon erecting the tube in the cistern, the top of the column presents a certain curve, the meniscus, the character of which is dependent on the composition of the glass and diameter of the tube. If now a bubble of air be introduced, and then removed by carefully causing the mercury to sweep up and down the length of the tube, upon erecting the barometer the mercury will stand at the same elevation as before, but the meniscus will be less convex. Here, as in the case of the bead, it may be conceived that the mercury and water have condensed an infinitely thin layer of air upon their surfaces, which provide for the phænomena of the spheroidal state in the latter instance, and which modify the affinity of the mercury for the glass in the former*.

Of this class of facts, to none has more interest attached than to

* The condensation of gases upon the surfaces of solids is a familiar fact, of which the ignition of a jet of hydrogen by platinum-sponge is a well-known illustration.

the recent experiments of Boutigny with molten metals. To him are we indebted for the first scientific consideration of this subject, although it appears that jugglers performed the feat of washing the hands in molten lead many years ago. Eleven years ago the author witnessed an explosion from the contact of molten slag with water, which expended most of its force upon the face and breast of a workman near. The shock prostrated and bruised, but did not burn him.

One form of the experiment is given in the adjustment of the wick of a burning spirit-lamp with the fingers, which is every day practised by chemists.

In the experiment of passing the hand into molten iron, which has been repeatedly performed by the author without discomfort, it is necessary only, as has been noticed by Boutigny and others, that the surface of the skin be wet, or covered with some body like powdered resin, which upon the application of heat will readily vaporize. That the experiment may be safely performed, any one may satisfy himself by passing through the molten mass any highly-combustible substance previously moistened, as for example a stick of sealing-wax. When the hand, previously moistened, is passed into the liquid metal, the water is vaporized, interposing between the metal and the skin a sheath of vapour. In its conversion into vapour the water absorbs heat, and this still further protects the skin. It was thus in the case of the workman alluded to above. His face was streaming with perspiration, and the molten slag came in contact, not with the skin, but with the layer of vapour which rose upon its surface as the heated mass came near.

The explanation of Berzelius, offered some years since, and confirmed by all the experiments, so far as I know, that have been performed, is the following:—

In the Leidenfrost experiment, a layer of vapour continuously evolved from the inferior surface of the liquid, provides an aëriform medium which does not conduct heat, but merely transmits radiant heat, which, passing through the liquid, as through most transparent substances, heats it but slightly. Thus evaporation is slow. The temperature of the liquid, it is well known, remains constantly below that of the boiling-point. This accounts for the much greater length of time required for water to evaporate when resting upon an oiled surface than when in contact with wood or metal; and for the length of time that dew-drops on spiders' webs will sustain exposure to the sun, when compared with that which would be required to evaporate an equal quantity of water from a surface where there is actual contact over a considerable area, and where conduction may take place.

The explosions sometimes following the first contact of a piece of potassium or sodium with water are due to the admixture of evolved hydrogen and atmospheric air. The explosion at the conclusion of the burning of the potassium or sodium is of another character. It is due to the sudden contact of the hydrate of potash when the temperature has become sufficiently low to permit it, and is analogous

to the phænomenon witnessed when the surface supporting a mass of water in the spheroidal state is permitted to cool down until contact takes place.

The explosions occasionally witnessed where a large quantity of fused saltpetre has come in contact with water, are of this description.

The explosions of steam-boilers have recently, in several instances, been ascribed to the properties of steam evolved from water in the spheroidal state, or evolved at the instant contact between the water and boiler is resumed. This is called a highly explosive steam. Not an experiment has been made, of which the author is aware, going to show any difference between this and ordinary steam. It is conceived, that, in some way, the mass of water in a boiler becomes separated from the interior surface of the metal, as in the experiment of Leidenfrost; and that upon cooling down to about 280° to 300° F. contact is resumed, and from the sudden evolution of steam, explosion results. But boilers of ordinary strength would sustain any pressure which could be exerted from steam, produced within its own walls at a temperature of 300° F.; and by the conditions supposed, the water in the boiler has been already more highly heated; else it could not have been *cooled down* to this temperature. A higher heat must have subjected the boiler to greater pressure, and yet that increased pressure had been sustained.

✓ *On the Chemical Composition of Quinoa Seed. By* Dr. Augustus Voelcker, *Professor of Chemistry in the Royal Agricultural College, Cirencester.*

The botanical name of the plant from which the small and mealy quinoa seeds are derived, is *Chenopodium Quinoa*. It belongs to the natural order of the *Chenopodiaceæ*, of which spinach and beet may be taken as the more familiar representatives. *Chenopodium Quinoa*, like all *Chenopodiaceæ*, is an apetalous plant, with minute green herbaceous flowers, appearing in close clusters towards the ends of the branches. In good lands it grows upwards of three feet, and produces small white or dark-coloured seeds, which, ground down to flour, furnish a nutritious article of food to millions of people. Though the leaves furnish a wholesome vegetable, similar to spinach, it is chiefly on account of the farinaceous seed that the plant is cultivated in many parts of South America.

There appear to exist several varieties of quinoa seed, differing in colour, size and taste from each other. The most common kind is a round, farinaceous, small seed, of the size of millet, and possesses an agreeable taste and no perceptible smell. Crushed between stones, it is reduced to meal, which is used by the Peruvians, boiled as soup or frumenty, very much in the same way as rice is prepared.

Quinoa meal makes very good porridge, puddings and cakes; but, like oats, it is unfit for the baking of bread.

Chenopodium Quinoa is not usually grown in this country; but as it is an exceedingly hardy plant, and furnishes a highly nutritious seed, as I am inclined to infer from the subjoined analyses, it might perhaps with advantage be planted in localities where cereals, and

even buckwheat, refuse to grow. For that reason I thought it not altogether superfluous to examine this seed, with a view to determine its nutritive powers. I am not aware of any analysis of quinoa; and as many people in South America are chiefly dependent on its use, the subjoined analysis, I trust, will not be altogether devoid of interest.

I have just mentioned that there are several varieties of quinoa. That which I analysed was grown on the estate of Mr. Milne, of Milnegraden, Berwickshire, who kindly furnished me with the material for the analysis. In its outer appearance this seed cannot be distinguished from the common quinoa; but its taste being slightly bitter and somewhat acrid, it is called bitter quinoa. The bitter taste however I found on experiment can easily be removed entirely by digesting the whole seed with a very dilute solution of carbonate of soda, which dissolves the bitter principle, the exact chemical nature of which I have not ascertained. My experiments lead me to regard the husk as the seat of the bitter principle.

When perfectly ripe, the seed is easily reduced to powder, and then furnishes a white meal with a tinge of yellow, which possesses no smell and a slightly bitter and rather acrid taste. Made into a dough with water, the mass is not rendered very elastic or tenacious, like wheaten flour under the same treatment. Quinoa meal in this respect resembles oatmeal, and for that reason it is unfit for the making of bread. Gluten, which gives tenacity and elasticity to the dough of wheaten flour, is retained on a piece of muslin when the dough is washed carefully with small portions of water at a time. The dough made of quinoa meal, treated in the same manner, leaves the impure husk of the seed on the muslin, which impure husk is not sticky, as it would be if it contained much gluten; and it appears therefore that quinoa seed contains but little gluten, if any. If the milky liquid which passes through the muslin, tied over a glass beaker, is allowed to settle until all starch has subsided at the bottom of the vessel, which requires several days, on account of the small size of the starch granules and the mucilaginous properties of the liquid, a clear slightly yellow fluid is obtained. Heated to the boiling-point of water, this clear liquid deposits a few flakes of coagulated albumen. These having been separated by means of a filter, a few drops of acetic acid produce an abundant, white, voluminous precipitate, showing the presence of a large quantity of soluble proteine compounds, analogous, if not identical, with legumine or vegetable caseine. I have not submitted this substance to an elementary analysis, and only studied its reactions with chemical reagents. These however distinctly proved that it was identical in this respect with a substance obtained under the same circumstances from oats, to which Professor Johnston has given the name of *Avenine*. Insoluble proteine compounds are likewise present in quinoa seed; and their presence is readily indicated by treating the impure husk remaining on the muslin by the washing process with a dilute caustic potash solution, filtration, and addition of acetic acid to the clear solution, when a white flaky precipitate will make its appearance. The powdered seed, boiled with æther, furnishes a yellowish

ætherial solution, which, after the æther has been distilled off, leaves a yellow, semifluid, fatty oil behind.

In the state in which the quinoa seed was obtained for analysis, it contained 16·017 per cent. of water.

My attention was first directed to ascertain the nutritive properties of quinoa meal. The nutritive qualities of farinaceous articles of food are usually and best determined by ascertaining the quantity of nitrogen, and calculating the amount of proteine compounds, on which their nutritive value chiefly depends, by multiplying the per-centage of nitrogen obtained by combustion with 6¼. I shall, therefore, in the first place, state the results of two nitrogen determinations:—

	I.	II.
Per-centage of nitrogen in the whole seed in its natural state (containing 16·017 of water)	3·19	2·95
Equal to proteine compounds	19·93	18·44
Average per-centage of nitrogen	3·07	
Equal to proteine compounds	19·18	

Quinoa seed, dried at 212° F., thus will contain in 100 parts—

	I.	II.	Average.
Nitrogen	3·80	3·52	3·66
Equal to proteine compounds	23·75	22·00	22·87

These two determinations correspond well with each other, the differences not being larger than those usually obtained in estimating the proportion of nitrogen in similar substances.

In the following table, the composition of the seed in its natural state, and dried at 212°, is represented:—

		Calculated dry.
Water	16·01	
Starch	38·72	46·10
Sugar and extractive matters	5·12	6·10
Gum	3·94	4·60
Oil	4·81	5·74
Caseine and a little soluble albumen	7·47	8·91
Insoluble albumen, and other proteine compounds	11·71	13·95
Vegetable fibre (husk)	7·99	9·53
Inorganic matter (ash)	4·23	5·05

On burning the seed, a white, very fusible and hygroscopic ash is obtained, which on analysis was found to consist in 100 parts, after deducting 9·74 sand, of—

Potash	33·18	36·76
Chloride of sodium	1·19	1·31
Lime	2·22	2·45
Magnesia	12·39	13·61
Oxide of iron	1·61	1·78
Phosphoric acid	35·20	38·99
Sulphuric acid	3·04	3·36
Silicic acid	1·98	2·19
Sand	a little	
Charcoal	9·74	

	I.	II.	Average.
Per-centage of ash in seed, containing 16·017 per cent. of water	4·27	4·19	4·23
Per-centage of ash in seed, dried at 212° F...	5·10	4·99	5·05

The above analyses suggest the following observations:—

1. The proportion of proteine compounds in quinoa seed is larger than in most cereals and starchy vegetable products. So far as the nutritive value of an article of food is dependent on this important class of bodies, quinoa meal deserves the preference before rye, barley, rice, Indian corn, plantain and potato, and is not inferior to the best samples of wheat and oats.

2. Quinoa seed approaches nearest in its composition to oats, with which it has likewise in common that it forms almost the only food of many people. This fact alone is sufficient to show that quinoa must contain everything requisite to support animal life in a healthy condition. The per-centage of proteine compounds in quinoa seed on which the sustenance of the muscles is supposed chiefly to depend, is even larger than in oats. The nature of the proteine compounds in quinoa is analogous, if not identical, with those in oats. Both contain, comparatively speaking, a large quantity of oil; and finally, the composition of the ashes of quinoa and oats shows a certain similarity.

3. Insofar as the supply of those mineral ingredients is concerned by which the body is supported, quinoa seed must be regarded as eminently fitted to sustain the strength of the human frame. The ash is rich in phosphoric acid and potash, and, like many seeds, more particularly farinaceous seeds, it contains a large proportion of phosphate of magnesia. Though exhibiting a general similarity with the ash of cereals, the above numbers show that the ash of quinoa approaches still closer that of peas and beans.—From the *Trans. of the Highland and Agricult. Soc. of Scotland*, October 1850.

Examination of the Root of Cephaëlis Ipecacuanha.
By E. Willigk.

The root of *Cephaëlis Ipecacuanha* was examined by Pelletier. He found in the bark of this root, fat, essential oil, wax, gum, starch, emetine, gallic acid, woody substance, and in the woody nucleus a peculiar extractive substance, together with the above-mentioned bodies with the exception of the wax. The author found, in his examination, small quantities of fat and a trace of an essential oil of disagreeable odour, with gum, starch, pectine, emetine, woody fibre and a new acid, which was erroneously considered by Pelletier to be gallic acid. The following are the results of this examination:—

Starch and Pectine.—When the pounded root is exhausted with boiling water, a brownish-coloured gelatinous liquid, of a disagreeable odour, is obtained, which was strained through coarse linen. The liquid separated in this manner from the woody fibre was diluted with a large quantity of water, and filtered through paper; it left on the filter a mucilaginous gray residue, which was difficult to wash, and dried into a blackish-brown, hard, brittle mass; on

boiling this with water, it furnished a yellowish liquid, in which the presence of starch was easily detected. On ebullition with water, to which a little ammonia had been added, a dark-coloured liquid was obtained, which deposited, upon the addition of muriatic acid, gelatinous flakes, which possessed all the properties of pectic acid.

Gum and Phosphates.—The filtered liquid contains a considerable quantity of gum, besides emetine and some salts. When the liquid is mixed with an aqueous solution of acetate of lead, a precipitate of a brownish colour falls, which on closer examination proved to consist for the greater part of phosphate of lead. The liquid filtered from this precipitate gives a fresh precipitate with tribasic acetate of lead; it was washed with water, and decomposed under water with sulphuretted hydrogen. The liquid filtered from the sulphuret of lead was evaporated to half its bulk, and mixed with an excess of alcohol of 0·803; a white substance fell, which was collected on a filter, washed, and dried at 212°.

It was easily soluble in water, furnished grape-sugar on being boiled with dilute muriatic acid, and left after combustion a fixed residue amounting to 1·14 per cent. The analysis gave 44·45 per cent. carbon and 6·31 hydrogen, which corresponds to the formula $C^{12} H^{10} O^{10}$, and represents the composition of gum. The peculiar acid of ipecacuanha is contained in the alcoholic liquid filtered from the gum. The liquid separated from the precipitate with tribasic acetate of lead deposits, on being mixed with strong alcohol, a lead salt of the gum, of white colour, which, decomposed by sulphuretted hydrogen, filtered from the sulphuret of lead, and evaporated to dryness, furnishes the largest quantity of the gum. The mother-liquors contain the emetine.

Ipecacuanhic Acid, $C^{14} H^{8} O^{6}$.—The powdered root was exhausted with boiling alcohol of 0·840, the filtered liquid precipitated with tribasic acetate of lead, the precipitate washed with alcohol of 0·830, and dissolved in dilute acetic acid. In this way the phosphate of lead is got rid of. The acetic solution was mixed with tribasic acetate of lead, and the precipitate collected on a filter. Some ammonia was added to the liquid separated from the precipitate, when a further deposit resulted. Both precipitates were, after being washed with alcohol of 0·803, suspended in æther, decomposed by sulphuretted hydrogen, and filtered from the sulphuret of lead. The first precipitate furnished a light yellow liquid, which was evaporated in the water-bath, in a current of dry carbonic acid, until the æther was expelled. The residue was mixed with water, filtered to remove any separated fat, and then digested with animal charcoal; the reddish-brown liquid filtered from the charcoal was evaporated to dryness in the water-bath in a current of carbonic acid. The residue, dried at 212°, was used for analysis; it is the hydrate of ipecacuanhic acid. The results of the analysis are given below. The second precipitate was treated like the first; the analysis of the acid obtained from it, dried at 212°, gave nearly the same results, as seen in II.

Properties of the Acid.—This acid forms a reddish-brown mass,

of an excessively bitter taste, is very hygroscopic, dissolves in æther, and more readily so in alcohol and water. The dilute aqueous solution furnishes with neutral acetate of lead no precipitate; but with tribasic acetate of lead, a white precipitate with a shade of brown is formed, which readily absorbs oxygen from the air, becoming darker; it also becomes darker on being dried, even when access of air is prevented.

With a solution of perchloride of iron the pure acid strikes a green colour, even when strongly diluted. On the addition of ammonia, a violet colour is produced, and with an excess, an inky-black liquid, from which a blackish-brown precipitate subsides. Salts of silver and mercury are reduced by the acid; salts of the oxide of copper give no precipitate; but on the addition of ammonia, a dirty greenish-brown precipitate results. When a solution of the pure acid is mixed with an alkali and exposed to the air, it soon turns dark blackish-brown, with absorption of oxygen; this tendency to absorb oxygen is likewise possessed, although in a smaller degree, by the pure acid and its salts. When the acid is heated, it puffs up, gives off a penetrating odour of formic acid, and leaves a vesiculous cinder, which burns with great difficulty.

It dissolves with a brownish-red colour in concentrated sulphuric acid: on the addition of water, a product of decomposition of the acid is separated in gray flakes. It is dissolved by nitric acid with a dark reddish-yellow colour; on gently raising the temperature, a lively evolution of gas ensues, whilst the solution acquires a yellow colour. Analyses of the two above-described precipitates:—

	I.	II.			
Carbon	56·36	56·11	14 =	1050·0	56·37
Hydrogen	6·23	6·22	9	112·5	6·04
Oxygen	37·41	37·66	7	700·0	37·59

The composition of the anhydrous acid was ascertained by the analysis of its lead salt, which was prepared by moistening the root with alcohol of 0·803, and exhausting with æther, evaporating the æther to the fifth part, and boiling the residual liquid for a long time with water, when a fatty substance separated; it was filtered from this, mixed with alcohol of 0·803, and thrown down with an alcoholic solution of neutral acetate of lead. The precipitate was washed with alcohol of 0·803, and dried at 212°. The analysis gave 45·9 per cent. oxide of lead, and the organic substance in combination with it furnished—

Carbon.....	60·10	14 =	1050·0	60·00
Hydrogen	5·72	8	100·0	5·71
Oxygen	34·18	6	600·0	34·29

The Neutral Salt of Lead, $C^{14}H^{8}O^{6}$, PbO + HO, was obtained once in the following manner:—The root was digested in warm alcohol of 0·850; the filtered liquid mixed with an alcoholic solution of neutral acetate of lead, filtered from the precipitate, and mixed with much water, then precipitated with tribasic acetate of lead, washed with cold water, and dried at 212°. It was of a brown colour. Analysis gave—

Carbon.....	32·07	14 =	1050·0	32·24
Hydrogen	3·43	9	112·5	3·45
Oxygen	21·85	7	700·0	21·50
Oxide of lead ..	42·65	1	1394·5	42·81

An *Acid Lead Salt*, $6(C^{14}H^{8}O^{6})+5PbO+4HO$, was obtained in the following manner:—The root was exhausted in the cold with alcohol of 0·830, the filtered liquid precipitated with an alcoholic solution of neutral acetate of lead, and the precipitate washed with alcohol, then dissolved in cold dilute acetic acid, filtered from the residue, and precipitated with tribasic acetate of lead. The precipitate was suspended in water, decomposed with sulphuretted hydrogen, the liquid filtered from the sulphuret of lead, again precipitated with tribasic acetate of lead, the precipitate washed with water, and dried at 212°. When reduced to a fine powder, it had a brownish-yellow colour. The analysis gave the following composition:—

Carbon.....	35·06	84 =	6300·0	35·15
Hydrogen	3·84	52	650·0	3·63
Oxygen	22·26	40	4000·0	22·31
Oxide of lead ..	38·84	5	6972·5	38·91

I have described below the preparation and analyses of two basic salts of lead. The first was obtained by exhausting the root with cold alcohol of 0·830, filtering, and precipitating the liquid with a spirituous solution of acetate of lead. The liquid filtered from the precipitate was thrown down with tribasic acetate of lead, the deposit washed with alcohol, dissolved in cold, dilute acetic acid, filtered from a residue of phosphate of lead, precipitated with alcohol of 0·803, and dried at 212°. The salt was brown. It gave on analysis the following numbers:—

Carbon	26·79	28 =	2100·0	26·94
Hydrogen.....	2·83	17	212·5	2·72
Oxygen	16·82	13	1300·0	16·68
Oxide of lead ..	53·56	3	4183·5	53·66

The second basic lead salt was prepared in the same manner; it had the following composition:—

Carbon	30·19	30·14	84 =	6300·0	30·10
Hydrogen	3·33	3·26	54	675·0	3·22
Oxygen	19·65	19·77	42	4200·0	20·06
Oxide of lead ..	46·83	46·83	7	9761·5	46·62

A solution of the pure acid, prepared from another quantity of the root, was precipitated with tribasic acetate of lead; the precipitate, dried at 212° and analysed, gave the following numbers for the organic matter combined with lead:—

Carbon.....	56·36	14 =	1050·0	56·37
Hydrogen	6·07	9	112·5	6·04
Oxygen	37·57	7	700·0	37·59

The compounds described correspond therefore to the following formulæ:—

Hydrate of ipecacuanhic acid .. =	$C^{14}H^{8}O^{6}+HO$
First lead salt.....	$C^{14}H^{8}O^{6}+PbO+HO$
Second lead salt.....	$6(C^{14}H^{8}O^{6})+5PbO+4HO$
Third lead salt	$2(C^{14}H^{8}O^{6})+3PbO+HO$
Fourth lead salt.....	$6(C^{14}H^{8}O^{6})+7PbO+6HO$.

The analyses of the hydrated acid and of the different lead compounds prove that the acid contained in ipecacuanha is not gallic acid, but a peculiar new acid. In composition, and also in some reactions, for instance with persalts of iron, it is closely related to caffeotannic acid; the occurrence of which in several plants of the *Rubiaceæ*, especially in the berries of *Coffea Arabica* and the root of *Chiococca racemosa*, has already been shown. It only differs from this acid in containing 1 equiv. of oxygen less:—

Caffeotannic acid ..... =	$C^{14}H^{8}O^{7}$
Ipecacuanhic acid (anhydrous)....	$C^{14}H^{8}O^{6}$

By the discovery of this acid, the series of those acids which have been found in different plants belonging to the family of the *Rubiaceæ*, has received the addition of a new member, as shown by the following formulæ:—

Catechine from *Nauclea Gambia* (dried *in vacuo*) =	$C^{14}H^{9}O^{9}$
Kinic acid (in its lead salt)	$C^{14}H^{8}O^{8}$
Caffeotannic acid (dried at 212°)	$C^{14}H^{8}O^{7}$
Ipecacuanhic acid (anhydrous)	$C^{14}H^{8}O^{6}$

Proc. Vienna Academy.

On the Compounds of Iodine with Quinine and Morphine.

By F. L. Winckler.

Equivalents of iodide of potassium and sulphate of quinine dissolved in boiling water furnish regular crystals of sulphate of quinine free from iodine; and similar results are obtained when other salts of quinine with oxyacids are employed instead of the sulphate. Very different results are obtained with the hydracids. Equivalents of muriate of quinine and iodide of potassium deposit a small quantity of a turpentine-like precipitate of iodide of quinine. Further experiment showed that, to decompose the muriate of quinine, 4 equivs. of iodide of potassium are requisite, and there is then produced a compound of—

Iodide of Quinine, $Ch^{2}I$.—This compound has, when dry, the properties of a resin; after cooling, it is very easily reduced to powder, without becoming electric on friction, like pure quinine; and it furnishes a perfectly white inodorous powder, of an extremely bitter taste, which does not alter in the air. The compound is more soluble in water than the sulphate of quinine, and almost in every proportion in alcohol and in æther; all the solutions are perfectly clear, colourless, and leave on evaporation the iodide of quinine in the form of a transparent resin. The salt is instantly decomposed, with elimination of iodine, by concentrated sulphuric and nitric

acids, and by chlorine; when burnt upon platinum foil, it left not a trace of potash; the cinder is difficult to burn. It furnished on analysis—

Quinine	71·58	2	= 4111·024	72·166
Iodine	28·42	1	1585·570	27·834

Iodide of Morphine, MoI, is obtained by dissolving 120 equivs. of dry acetate of morphine in 8 times the weight of cold distilled water, adding if necessary a few drops of pure acetic acid, and mixing the filtered solution with a solution of 60 equivs. of iodide of potassium. After some time the salt crystallizes out in very slender crystals, which however are obtained of much larger size when the mixture is heated on the water-bath, and is allowed to cool slowly. In this manner it is obtained in transparent, shining, colourless, four-sided prisms, which cannot be distinguished from those of the sulphate of quinine. Indeed in the dry state it would be perfectly impossible to distinguish between these two compounds without the aid of chemical reagents.

Iodide of morphine is not perceptibly soluble in cold water; it dissolves abundantly in hot water and readily in alcohol; the solutions have a very bitter taste. Analysis gave—

Morphine.....	71·4	1	= 3927·0	71·24
Iodine	28·6	1	1585·6	28·76

The author draws attention to the probably important medicinal properties of these compounds.—*Jahrb. für Prakt. Pharm.*, xx. p. 321.

Analysis of a Combination of Ammonio-chloride of Nickel with Ammonio-nitrate of Nickel. By R. Schwartz.

This compound, for which the author obtained the formula $(3NH^3, NiCl)+6(2NH^3, NiO, NO^5, HO)+10HO$, crystallizes in azure-blue octahedra of considerable size, becomes somewhat moist in the air without deliquescing, and smells slightly of ammonia. The salt deflagrates upon charcoal; heated in a glass tube above its melting-point, it loses at first water and ammonia, and subsequently nitric acid as hyponitric acid, with a violent explosion. It dissolves pretty readily in water; the solution becomes turbid from eliminated oxide of nickel. A great portion of the oxide of nickel and the ammonia are separated by ebullition. It consists of:—

Nitric acid.....	31·6	6	= 324·0	31·9
Nickel	20·1	7	206·5	20·3
Chlorine	2·8	1	35·5	3·5
Nitrogen	20·2	15	210·0	20·7
Hydrogen	6·4	61	61·0	6·0
Oxygen	17·5	22	176·0	17·3

Proc. Vienna Academy.

PROCEEDINGS OF SOCIETIES.

Royal Society.

June 20, 1850.

"On the Condition of certain Elements at the moment of Chemical Change." By B. C. Brodie, Esq., F.R.S.

This paper contains an experimental inquiry, founded upon certain theoretical considerations as to the condition of bodies at the moment of chemical change, with the discussion of which the introduction is occupied.

The author considers that the peculiar combining properties of the elemental particles of which chemical substances are composed, are due to a chemical polarity of the acting masses, which takes place at the contact of the bodies, and have only a remote relation to the electro-chemical nature of the isolated element. In support of this view are cited the phænomena of double decomposition, and the properties of the so-called "nascent" elements, which could never be inferred from the nature of the element when once isolated and formed. Double decomposition the author considers to be the true type of all chemical action. In the case of the bodies called compound, this polarity is manifested by the division of the substance into two parts, which are universally considered to stand to one another in a certain positive and negative relation; and also by the synthesis, which corresponds to this division.

The object of the paper is to point out that an analogous polar relation exists, at the moment of chemical change, between the particles of which the elemental bodies themselves are composed, of which condition we have evidence both when the isolated element is chemically acted on by other bodies, and also in certain cases of the formation of the element from its compounds, in which we have a division and synthesis of the element corresponding (so far as this polar relation is considered) to the division and synthesis of a compound body. The evidence of these statements is, that when the isolated element is chemically acted upon, we may observe in it (as manifested by its combining properties) the same polar or nascent state as is developed in compound bodies; and also that we have certain remarkable cases of the synthesis of the element, to account for which we must assume the same combining relation between its particles as between the particles of which a compound substance is formed. These statements are supported by numerous instances.

The experimental inquiry relates to a remarkable case of the formation of oxygen, in which the author considers that the mutual attraction of the particles of that element determines the decomposition of the substances from which it is evolved. The experiment in question is the mutual decomposition which the peroxide of hydrogen and certain metallic oxides, first discovered by Thénard, undergo when in contact. Thus the author regards, in this case, the decomposition of the metallic oxide as a phænomenon which may be represented thus:—

$$HO_2 + mO_2 = \overset{+\ -\ +\ -\ +\ -}{HOOOOm} = HO + O_2 + mO,$$

the metallic peroxide being reduced by the polar particle of oxy-

gen, as in other cases it might be by hydrogen itself. The proof that such a chemical relation really exists between the particles of oxygen, would be found in the proportion in which the two substances were reduced. The paper contains an elaborate inquiry on this point in the case of the chloride and of the oxide of silver; the general result of which is, that these substances are capable of being reduced in various but definite proportions, according as the conditions of temperature and mass are varied. All the terms of this series of ratios have not been determined; but it is ascertained that the relative loss for the two substances proceeds by intermittent steps, and that the whole action is confined between the limits of the ratio of equality on the one hand, and the purely catalytic action (in which the metallic oxide would suffer no reduction) on the other; neither of which limits is ever absolutely reached.

The constant loss of oxygen from the decomposing bodies in equal equivalent proportions is found in the reaction of the peroxide of barium with iodine in the presence of water. In this experiment, the water in the presence of the iodine is reduced just as the peroxide in the other experiments; but here the loss is constant, and the change may be represented thus:—

$$\underset{\overset{-+-+-+}{\text{IHOOOBa}}}{\text{IHOOOBa}} = \text{IBa} + \text{HO} + \text{O}_2.$$

In this experiment no oxide of iodine whatever is formed, and the author considers that the formation of the oxygen itself is here the corresponding fact to the formation of the iodous acid, which takes place when iodine acts upon baryta.

January 30, 1851.

"On the Oxidation of Ammonia in the Human Body, with some remarks on Nitrification." By Henry Bence Jones, M.D., F.R.S. &c.

The author having shown, in a paper lately communicated to the Royal Society, that the effect of tartrate of ammonia on the acidity of the urine was totally different from that of tartrate of potash, and that carbonate of ammonia, taken in very large quantities, did not produce any alkaline reaction of the urine, but that, on the contrary, the acidity was rather increased than diminished by such doses, repeated the experiments with carbonate of ammonia, hoping to obtain more decided results. Although, from these experiments, it was again apparent that no diminution of the acid reaction resulted from taking carbonate of ammonia, yet the fact of any great increase in the acidity of the urine could not be determined. In his former paper, the author suggested that an inquiry into the occurrence of nitric acid in the urine would probably give the solution of this unexpected effect of carbonate of ammonia; and he was led to undertake the experiments described in the present paper with the view of detecting the presence of that acid under particular circumstances.

The indigo test for nitric acid being more delicate than the protosulphate of iron test, it was chiefly employed; but a mixture of starch with a drop or two of hydriodate of potash and hydrochloric

acid was found to be a far more delicate test than either. Beginning with 10 grs. of nitrate of potash added to 10 oz. of urine, it was found at last that as little as 1 gr. of nitre to 10 oz. of urine could be detected with the greatest certainty and clearness when the starch test was used; but this quantity could not be detected as surely by the indigo test.

Experiments are described in which carbonate of ammonia was given, in doses varying from 40 grs. to 7 grs., to a healthy man in whose urine no nitric acid could previously be detected; and the urine was tested at intervals of several hours after each dose. From these it appears that 10 grs. was the smallest quantity that gave decided evidence of nitric acid by both tests.

Having satisfied himself that when carbonate of ammonia was taken small quantities of nitric acid passed off in the urine, the author made similar experiments with tartrate of ammonia, administered in doses of 60 and 40 grs.; and in each case the starch test gave evidence of the presence of nitric acid in the urine some hours after. Similar experiments with the muriate of ammonia are next described; and in these the presence of nitric acid in the urine was readily detected three hours after the administration of the dose, even when it was so small as 10 grs.

From an experiment described in the paper, it was shown, that by a simple combustion of ammonia out of the body, as well as in the body, nitric acid was produced. From other experiments it appears that urea, also, by oxidation, whether in the body or out of the body, gives rise to nitric acid.

Having found that nitric acid was produced more readily and frequently than had been supposed to be the case, the author was led to try whether combustions in the atmosphere without ammonia could not give nitric acid. The presence of this acid was, in consequence, detected in the products of the combustion of alcohol, of coal, of a wax candle, and of hydrogen.

As this led to the supposition that nitric acid might exist in rain-water at all times, experiments were made on the rain-water collected on wet days in London, and the presence of nitric acid was discovered by the starch and also by the indigo test.

The conclusions the author comes to from his experiments are:—

1. That the action of oxygen takes place in the body, not only on hydrogen, carbon, sulphur and phosphorus, but also on nitrogen.

2. That in all cases of combustion, out of the body and in the body, if ammonia be present, it will be converted partly into nitric acid.

3. That the nitrogen of the air is not indifferent in ordinary cases of combustion, but that it gives rise to minute quantities of nitric acid.

He further remarks, that the production of nitric acid from ammonia in the body adds another to the many instances of the action of oxygen in man; and that the detection of nitric acid in the urine may lead to the conclusion, that the blood is being freed from ammonia, or from substances closely related to it, as urea, or possibly caffeine and other alkaloids.

THE CHEMICAL GAZETTE.

No. CCIV.—April 15, 1851.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Products of the dry Distillation of Sugar with Lime.

By R. Schwartz.

Fremy found that the liquid product which is obtained by the distillation of 1 part sugar or starch with 8 parts anhydrous lime consists of a portion soluble in water, and an insoluble one. He found the composition of the portion soluble in water to correspond to the formula $C^6 H^6 O^2$, and declared it to be identical with acetone. The insoluble portion consists, according to his researches, principally of a substance which boils at 183° F., and is represented by the formula $C^6 H^5 O$; he gave it the name of metacetone. According to this, this substance would have the same per-centage composition as Kane's oxide of mesityle. Besides these products, there is formed, according to Fremy, in this process of decomposition, mere traces of combustible gases. Gottlieb found, that, instead of 8 parts of lime, it was more advantageous to use 3 parts to 1 part of sugar; and that in this manner a few ounces of pure metacetone might be easily prepared. He obtained, in the oxidation of this substance with chromic acid, formic, acetic and metacetonic acids.

The author distilled considerable amounts of sugar, both with 8 and with 3 parts of lime. The liquid product which passed over, with disengagement of combustible gas, was mixed with water, and again submitted to distillation. A comparatively small quantity of some resinous bodies was left in the retort, whilst a slightly yellow oil, of a peculiar odour, distilled over with the water. It was frequently agitated with water, in which a portion dissolved; the insoluble portion proved, on closer examination, to be a mixture of different substances, difficult to isolate. It was found, that, on being shaken with a cold aqueous solution of potash, it decreased in quantity, whilst the potash acquired a dark brownish-red colour. When this washing with caustic potash was frequently repeated, and the oil afterwards agitated with water to remove any potash it might contain, a very mobile fluid, of far more agreeable ætherial odour than the original product, was obtained, which, on being now shaken with dilute caustic potash, experienced no further perceptible alteration. The purified substance, exposed to the oxygen of the air, soon acquired anew the property of imparting a dark colour to a solution of potash. This volatile product, purified with solution of potash, is not a simple compound, but a mixture of several, which

it was attempted to separate by fractional distillation. For this purpose, the purified oil, which had been previously freed from the portion soluble in water, and had been treated with aqueous solution of potash, was distilled from a vessel placed in boiling water as long as anything passed over at that temperature. The residue of this distillation was heated in an oil-bath at 248°, and the distillate collected fractionally.

By collecting the products which passed over between 248° and 320°, as also between 320° and 392°, and finally that between 392° and 482°, separately, a residue was obtained, which was no longer volatile at this temperature, and which, in order to avoid any decomposition at so high a temperature, was mixed with a large proportion of water, and again submitted to distillation. These separately-collected portions are mixtures of liquids, whose boiling-points are situated very close together. By fractional distillation of each of these several portions, the author succeeded in isolating a number of compounds, whose composition, ascertained by analysis, shows them to be members of a series which differ from each other by 2 equivs. carbon and 2 of hydrogen, which each member contains more than the next lowest. The empirical formulæ of these substances, as calculated from the results of the analyses, are—

$C^{14}\,H^{11}\,O^{3}$	$C^{17}\,H^{20}\,O^{3}$
$C^{15}\,H^{15}\,O^{3}$	$C^{20}\,H^{25}\,O^{3}$

With the increase of the amount of carbon and hydrogen in these compounds, the boiling-point rises so that the substance $C^{14}\,H^{11}\,O^{3}$ is the most volatile. In the series enumerated, the members corresponding to the formulæ $C^{16}\,H^{13}\,O^{3}$, $C^{22}\,H^{19}\,O^{3}$, $C^{24}\,H^{21}\,O^{3}$ and $C^{26}\,H^{23}\,O^{3}$ are wanting.

All these substances agree in this respect, that they are indifferent, and are decomposed in the same manner by boiling with concentrated aqueous solution of caustic potash.

When a mixture of these different bodies is treated with oxidizing agents, a distillate is obtained in which fatty acids occur. When the most volatile portion is not employed for this oxidation, not a trace of formic acid is formed. At the same time with the fatty acids, the distillate contains an indifferent ætherial substance. When the different substances of this series, whose composition may be expressed by the general formula $C^{n}\,H^{n-3}+O^{3}$, is heated to boiling with concentrated caustic potash in an apparatus so constructed that the volatile portion must always flow back into the retort, it undergoes a change; a certain amount of resins is produced, which dissolve with a dark brown colour in the alkaline liquid, and separate from it in part as a black mass, whilst upon the dark-coloured solution of potash, a more volatile, very mobile substance floats, which, when the action of the potash is finished, may be separated by distillation, and then forms a very mobile fluid of an agreeable odour, possessing the narcotic effects of æther and chloroform when inhaled in a high degree. When these compounds of the series $C^{n}\,H^{n-3}+O^{3}$ are treated with oxidizing agents, for instance chromic and nitric acids,

after they have been acted upon by potash, no fatty acids are obtained, with the exception of a mere trace of metacetonic acid; but oxalic acid, and a volatile oil identical with that which was formed, together with a certain amount of fat acids in the oxidation of the members of the series $C^n H^{n-3} + O^3$, before its treatment with boiling solution of potash. Consequently, by the treatment with boiling potash, the so-called metacetone has been deprived of the source from which on its oxidation the fat acids were formed.

If we consider the composition of the entire series of these substances whose general formula is $C^n H^{n-3} + O^3$, they may be decomposed into two formulæ, as shown below, where those which have already been isolated have an * affixed:—

$$
\begin{aligned}
*C^{14}\,H^{11}\,O^3 &= C^{12}\,H^9\,O + C^2\,H^2\,O^2\\
C^{16}\,H^{13}\,O^3 &= C^{12}\,H^9\,O + C^4\,H^4\,O^2\\
*C^{18}\,H^{15}\,O^3 &= C^{12}\,H^9\,O + C^6\,H^6\,O^2\\
*C^{20}\,H^{17}\,O^3 &= C^{12}\,H^9\,O + C^8\,H^8\,O^2\\
C^{22}\,H^{19}\,O^3 &= C^{12}\,H^9\,O + C^{10}\,H^{10}\,O^2\\
C^{24}\,H^{21}\,O^3 &= C^{12}\,H^9\,O + C^{12}\,H^{12}\,O^2\\
C^{26}\,H^{23}\,O^3 &= C^{12}\,H^9\,O + C^{14}\,H^{14}\,O^2\\
*C^{28}\,H^{25}\,O^3 &= C^{12}\,H^9\,O + C^{16}\,H^{16}\,O^2
\end{aligned}
$$

In these formulæ they appear as a series of compounds analogous to the compound æthers; they are combinations of a substance of similar nature to the oxide of æthyle or methyle with the aldehyde of a fat acid. This view explains very simply the occurrence of fat acids in the oxidation of these bodies, the aldehydes passing, by the assimilation of 1 equiv. of oxygen, into the corresponding acid. It also explains the occurrence of resinous products in the treatment with the boiling solution of potash, the aldehydes being resinified, whilst the body $C^{12} H^9 O$, analogous to the oxide of æthyle or methyle, at the moment of its being eliminated by a more powerful base from its combination, takes up 1 equiv. of water, and is converted into the corresponding alcohol. It further results from this view, that these combinations of the aldehydes with the body $C^{12} H^9 O$ must furnish on oxidation, besides the fat acids, an indifferent product, identical with that which is produced when the body $C^{12} H^{10} O^2$, formed by the action of alkalies, is treated separately with oxidizing substances. The constitution here assumed of these compounds likewise explains their behaviour towards concentrated sulphuric acid and anhydrous phosphoric acid, by whose action the aldehydes are decomposed, and, by the removal of hydrogen and oxygen in the proportion in which they form water, the final product, $C^{12} H^8$, is obtained.

It has already been mentioned, that the distillate obtained from sugar and lime left on rectification a small quantity of resinous products. These were shaken with milk of lime, filtered from the excess of hydrate of lime, evaporated, and the residue distilled with dilute sulphuric acid; the product was saturated with barytic water and concentrated in the water-bath. The syrupy residue was mixed with alcohol, and the salt thereby precipitated employed for analysis

after being dried at 212°. The following results correspond to the formula $C^{20} H^{17} O^{13} + 5BaO = 2(C^{10} H^{8} O^{6} + 2BaO) + BaO, HO$, in which $C^{10} H^{8} O^{6}$ expresses the composition of the anhydrous metacetonacetic acid :—

Carbon	18·82	20 =	120·0	19·22
Hydrogen	2·72	17	17·0	2·72
Oxygen	16·43	13	104·0	16·69
Baryta	62·03	5	383·0	61·37

It was likewise stated above, that the product of the distillation of sugar and lime after its rectification was first agitated with water in order to free it of acetone; and that, on being mixed with cold aqueous solution of potash, it decreased in volume, and coloured the solution a dark red-brown, thus showing the presence of a compound behaving in a similar manner to aldehyde. This acrid and disagreeably-smelling substance, which is removed by the treatment with potash, is decomposed in this operation into three different products. The brown potash solution was mixed with sulphuric acid, and submitted to distillation. A quantity of a brown resin separated, to which was owing the brown-red colour of the potash-solution. The slightly-acid distillate was mixed with barytic water and distilled. The product contained an oil of a peppermint smell, which was partly dissolved in water, and partly floated on the surface of the liquid. It was separated from its solution in water by saturating the liquid with chloride of calcium, drawing it off with a pipette, and dried over fused chloride of calcium. It gave on analysis—

Carbon	61·07	6 =	36	61·01
Hydrogen	12·10	7	7	11·86
Oxygen.....	26·83	2	16	27·13

In this substance the carbon and hydrogen are in the same proportion as in glycerine. Moreover, the æther corresponding to metacetonic acid must likewise contain the carbon and hydrogen in the proportion of 6 : 7. Adopting for the substance the formula $C^{6} H^{7} O^{2}$, it may be regarded as the hydrate of the oxide of acetonyle, or $C^{6} H^{7} O^{2} = C^{6} H^{6} O + HO$.

The barytic liquid from which this oil had been distilled was mixed with sulphuric acid, and submitted to a fresh distillation; a faintly-acid liquid passed over, which contained so small an amount of fat acids that it was impossible to determine its composition by further experiments. It results from all these experiments, that among the products of distillation of sugar with lime, one or several aldehyde-like substances are produced, which, on treatment with caustic potash under the influence of the air, are decomposed into resinous products, which remain combined with the potash; whilst at the same time small quantities of acids are formed, which likewise enter into combination with the potash. As a collateral product of this process of transformation, an indifferent substance is formed, viz. the oil with the peppermint odour above mentioned.

On agitating the products of the distillation of sugar and lime

with water, a portion is dissolved. Fremy stated that the water took up acetone, which the author confirms. After treating the crude metacetone with water, aqueous solution of potash, and subsequent washing with water, the mixture of the different substances mentioned above under the formula $C^n H^{n-3} + O^3$ remain. The analysis of these substances, separated by fractional distillation, gave the following numbers:—

The portion distilled off at 158° F.—

Carbon	70·17	70·42	14 =	84	70·58
Hydrogen	9·48	9·57	11	11	9·24
Oxygen	20·35	20·01	3	24	20·18

The portion distilled off at 203°—

Carbon	73·82	73·63	18 =	108	73·46
Hydrogen	10·31	10·20	15	15	10·20
Oxygen	15·87	16·17	3	24	16·34

The portion distilled off at 302°—

Carbon	74·37	74·42	20 =	120	74·53
Hydrogen	10·10	10·19	17	17	10·55
Oxygen	15·53	15·39	3	24	14·92

The portion distilled off at 392°—

Carbon	77·50	77·73	28 =	168	77·41
Hydrogen	11·04	11·54	25	25	11·52
Oxygen	11·46	10·73	3	24	11·07

The mixture of these compounds yields, on oxidation with chromic acid, as already observed by Gottlieb, formic, acetic and metacetonic acids. The author likewise obtained at the same time a volatile oil, which was not acid, and had the formula $4(C^{10} H^8 O) + HO$, as evident from the following analysis:—

Carbon	76·60	40 =	240	76·67
Hydrogen	10·48	33	33	10·54
Oxygen.....	12·92	5	40	12·79

When the mixture of the compounds of the formula $C^n H^{n-3} + O^3$ is heated to boiling with concentrated solution of potash in an apparatus in which the condensed liquid must constantly flow back into the vessel, and this treatment is continued as long as the potash exhibits any action; and if the volatile product floating upon the dark brownish-black coloured solution of potash is distilled off, a very mobile colourless substance is obtained, which on inhalation produced the effects of chloroform and æther in a high degree, and, dried over chloride of calcium, gave—

Carbon	72·01	60 =	360	72·14
Hydrogen....	10·61	51	51	10·22
Oxygen.....	17·38	11	88	17·64

A second preparation gave—

Carbon	73·46	6 =	36	73·46
Hydrogen.....	10·08	5	5	10·20
Oxygen.....	16·46	1	8	16·34

This compound was heated with moderately-concentrated nitric acid, and furnished a pretty considerable quantity of oxalic acid, and a volatile body which agreed in all its bodies with that already described above with the formula $4(C^{10}H^8O)+HO$. After being dried over fused chloride of calcium, it furnished the following results:—

Carbon	78·68	10 =	60	78·94
Hydrogen	10·59	8	8	10·52
Oxygen	10·73	1	8	10·54

The production of the compound $C^{10}H^8O$ from the body $C^{12}H^{10}O^2$ is explained simply by the elimination of the group C^2H^2O. This group yields, on the oxidation of its hydrogen, oxalic acid.

When the compound $C^{12}H^{10}O^2$ is treated with concentrated sulphuric acid or with anhydrous phosphoric acid, oxygen and hydrogen are removed in the form of water; and if a sufficient quantity of these agents be employed, a product free from oxygen is obtained. It contains 6 equivs. carbon to 4 equivs. hydrogen, forms a limpid oil, which smells like the products of the destructive distillation or coal, distils over unaltered, and furnished on analysis the following numbers:—

Carbon	89·81	12 =	72	90·00
Hydrogen	10·28	8	8	10·00

It is highly probable that the substance $C^{12}H^{10}O^2$, before passing into $C^{12}H^8$, is converted into a compound, $C^{12}H^9O$; for in the treatment with anhydrous phosphoric or sulphuric acid, before the action has gone as far as the production of $C^{12}H^8$, products of an ætherial odour were obtained, the analysis of which rendered highly probable the existence of such a product. The numbers which were obtained, as well as the constant rise of the boiling-point in the distillation, showed that the substances were mixtures of the compound $C^{12}H^9O$ with unaltered $C^{12}H^{10}O^2$; and when the action of the phosphoric or sulphuric acid was continued further, it was impossible to avoid an admixture of $C^{12}H^8$. The substance $C^{12}H^9O$ is either identical or at least isomeric with that group of atoms which must be viewed in the crude acetone as the basic portion united with the aldehydes of different fat acids. The compound $C^{12}H^8$ may be prepared from the different members of the series $C^nH^{n-3}+O^3$ by treating them with concentrated sulphuric acid. A comparatively small amount of the hydrocarbon is formed from the group $C^{12}H^9O$, whilst the aldehydes which were combined with this group are destroyed by the sulphuric acid, and converted into a black resinous mass.

As the compound $C^{12}H^{10}O^2$ contains carbon and hydrogen in the same relative proportion as the so-called allyle, some experiments were made with the view of replacing the oxygen by chlorine, in order to prepare from that compound the corresponding sulphocyanide and sulphuret. These experiments, made in order to produce oil of mustard and of horseradish, gave a negative result.—*Proceedings of the Vienna Academy.*

On the Action of Ammonia on the Oil of Rue, and some of the resulting Products. *By* Dr. R. WAGNER.

According to the investigations of Gerhardt and Cahours, the essential oil of rue (*Ruta graveolens*) is a mixture of a very small quantity of a hydrocarbon with an oxygenated oil, $C^{20}H^{20}O^2$, which was considered by the first chemist as the aldehyde of capric acid. By oxidation it forms an acid, $C^{20}H^{20}O^4$, to which Cahours applied the name of rutic acid. Gerhardt showed, by the analysis of the baryta salt and by several properties of the rutic acid, that it was identical with capric acid. The formation of oil of rue from cod-liver oil *, in which the presence of capric acid has been proved with tolerable certainty, likewise serves to confirm the intimate relations which exist between oil of rue and capric acid. That the oil of rue is, in fact, an aldehyde, is evident from its behaviour towards an ammoniacal solution of oxide of silver ; and its behaviour towards ammonia likewise proves that in this respect the oil of rue resembles acetic aldehyde.

When oil of rue is dissolved in alcohol, and ammoniacal gas is passed into the solution at a low temperature, a white crystalline mass is obtained, which differs from the solid oil of rue obtained by Cahours, as it melts at about 32° F., and is decomposed into oil of rue and ammonia. This body evidently corresponds to aldehyde-ammonia, and is a combination of capric aldehyde (oil of rue) with ammonia, $C^{20}H^{19}O, NH^4O$.

A portion of the substance was dissolved in alcohol, and a current of sulphurous acid gas passed into it. This liquid having been exposed for some days to a severe winter temperature, deposited some white shining plates, which appeared, after filtering the liquid and pressure between blotting-paper, as a bulky mass similar to margaric acid. The crystals are insoluble in water, but readily soluble in boiling alcohol; on ebullition with potash, ammonia and oil of rue are evolved; heated with dilute sulphuric acid, they give off sulphurous acid with separation of oil of rue. At a gentle heat they are decomposed, without previously melting. The author determined the amount of nitrogen and sulphur; that of the carbon and hydrogen could not be ascertained for want of material. The formula is probably $C^{20}H^{23}NO^6S^2$:—

Carbon		20 =	120	50·63
Hydrogen..... ..		23	23	9·70
Nitrogen	5·00	1	14	5·09
Oxygen..... ..		6	48	20·25
Sulphur.....	13·83	2	32	14·33

This compound must be regarded as a double salt, consisting of sulphite of ammonia and sulphite of the oxide of caprinyle; its rational formula is therefore $NH^4O, SO^2 + C^{20}H^{19}O, SO^2$.

According to this formula, the new substance is the bisulphite of capric aldehyde and ammonia, and homologous—

1. With taurine and the isomeric bisulphite of aldehyde-ammonia of Redtenbacher $= NH^4O, SO^2 + C^4H^3O, SO^2$.

* Chem. Gaz., vol. vii. p. 175.

2. With the bisulphite of œnanthylic aldehyde-ammonia of Tilly $=NH^4O, SO^2+C^{14}H^{13}O, SO^2$.

The bisulphite of capric aldehyde-ammonia is consequently the tenth member of that series of homologous compounds of which taurine and its isomeric body form the second and Tilly's compound the seventh.

Wagner further attempted to prepare the thialdine of the caprinyle series, and with this view passed sulphuretted hydrogen into a spirituous solution of oil of rue and ammonia. In the course of a few days some shining crystals had separated from the liquid, but were decomposed in the attempt to purify them by recrystallization. On ebullition with potash, oil of rue is eliminated from these crystals, with disengagement of ammonia. On supersaturating the liquid with dilute sulphuric acid, after the boiling had been continued so as to expel all essential oil, sulphuretted hydrogen was disengaged; consequently this compound contained oil of rue, ammonia and sulphuretted hydrogen.

If it be allowable to deduce by analogy, from the results of the qualitative examination, a formula for this substance, the formula $C^{60}H^{61}NS^4$ would be the most probable. In accordance with this, the substance would have an analogous composition to the thialdine of the acetyle series, and it might be called thiocaprinaldine. It would originate from the oil of rue and ammonia in the same manner as thialdine from aldehyde-ammonia—

$$3C^{20}H^{19}O, NH^4O+6SH=C^{60}H^{61}NS^4+2NH^4S+6HO.$$

Experiments to prepare a compound corresponding to Redtenbacher's carbothialdine from the oil of rue and ammonia by means of sulphuret of carbon, proved unsuccessful.

In conclusion, the author describes a reaction of oil of rue which points to the existence of an oxygen compound homologous with acetylous acid, and situated between the oxide of caprinyle, $C^{20}H^{19}O$, and capric acid, $C^{20}H^{19}O^3$. When oil of rue is boiled with an ammoniacal solution of nitrate of silver, a metallic mirror is formed; if the boiling is continued until no more silver is reduced, until therefore all the oil of rue is oxidized, we should expect to find in the solution, besides the nitrate of ammonia and excess of nitrate of silver, only caprate of silver. But when the solution separated from the metal is heated with excess of potash, and the resulting precipitate is exhausted with dilute sulphuric acid, some pulverulent metallic silver is left behind. Hence the solution might contain the silver salt of caprinylous acid, $C^{20}H^{19}O^2$, besides caprate of silver. When the alkaline solution filtered from the black precipitate is evaporated to dryness and the residue moistened with dilute sulphuric acid, it diffuses the odour of capric acid. The formation of the caprinylous acid, and the subsequent production of capric acid, may be explained by the following two equations:—

1. $C^{20}H^{19}O, HO+2AgO=C^{20}H^{19}O^2, AgO+Ag+HO.$
2. $C^{20}H^{19}O^2, AgO+KO=C^{20}H^{19}O^3, KO+Ag.$

If we had at our disposal large quantities of oil of rue, there is

no doubt that experiments to prepare from the oil of rue and ammonia the compound corresponding to Strecker's alanine, $C^{20}H^{23}NO^4$, and the acid homologous with lactic acid, $C^{22}H^{22}O^6$ ($C^{20}H^{19}O$, HO + C^2HO^3, HO), would furnish satisfactory results.—*Journ. für Prakt. Chem.*, liii. p. 48.

On the Volatile Acids of the Urine. *By* Dr. G. Stædeler.

The author remarks, that, in the same manner as we frequently succeed in obtaining a probable idea of the peculiar composition of an organic substance from the artificial products of its decomposition, so we also endeavour to ascertain from the components of the excretions of the living organism, which may be regarded as ultimate products of the blood and the materials of which the organs are composed, a knowledge of the constitution of these formative matters of the blood, and of the chemical processes which are in essential connexion with the phænomena of life. Hence matters constituting the secretions have repeatedly formed the object of chemical investigation; yet their volatile constituents have hitherto remained almost entirely disregarded, although a knowledge of them is not less significant in answering these important questions than the knowledge of the non-volatile constituents. In this physiological point of view, the author undertook the examination of the volatile constituents of the urine, which are at present almost entirely unknown.

Both in the urine of man and in that of the herbivora, two groups of acids and an indifferent nitrogenous substance may be shown to exist, the quantity of which however appears to vary in the different groups of animals to a great extent. Whilst in the case of the human urine the satisfactory detection of the various groups was alone possible, in that of the herbivora the greater number of the individual substances were separable in quantity sufficient for determining their elementary composition. As these volatile substances in general form a small portion only of the urine, large quantities of this secretion were required; and as the urine of cows was most readily procurable, this was principally used in the following experiments.

About 80 lbs. of the morning urine of cows, which during the day were pastured, and in the morning and evening were fed upon hay, straw and bran, were mixed with hydrate of lime, and after being once boiled, were poured off the lime, and evaporated to about one-eighth their volume at a boiling heat. The filtrate was then supersaturated with muriatic acid, whilst kept well cooled, and the hippuric acid which separated removed from the mother-liquor after standing for twelve hours. By distillation and repeated rectification, the volatile substances dissolved in the water were condensed; and ultimately an oily slightly-yellowish liquid, of a very repulsive odour, was obtained, which sank in the water which simultaneously passed over. The product amounted to about 30 grms. The varying specific gravity of this oily product and the reaction with solution of potash, which left a portion undissolved, gave rise to the conclusion,

that it consisted of a mixture of different bodies; distillation of the oil and water was therefore again had recourse to with a weighed quantity of hydrate of potash, when a light pale-yellow oil was obtained.

This oil, the odour of which was most comparable to that of a mixture of oil of rosemary and origanum, does not preexist in the urine, but is apparently a product of the action of potash upon the substance possessing the repulsive odour. Its reaction was neutral; it contained nitrogen; was dissolved by concentrated sulphuric acid with a deep red colour; and its aqueous solution was not precipitated by basic acetate of lead, nor reddened by perchloride of iron. Although more minute examination of this nitrogenous substance was so desirable, it was impossible on account of the small quantity obtained.

As the separation of the hippuric acid from the evaporated urine had been effected by means of muriatic acid, the acids combined with the potash must have included muriatic acid, as also benzoic acid resulting from the decomposition of the hippuric acid. To keep the latter back, five-sixths of the potash used were saturated with sulphuric acid, and distillation continued until no further precipitate was produced in the distillate by basic acetate of lead. The liquid obtained, the odour of which exactly resembled that of phenylic acid, was repeatedly subjected to fresh distillation, until the greater part of it was procured in an oily state, and a small quantity only of an aqueous liquid was left. As this exerted a strongly acid reaction, the layer of oil could not consist of phenylic acid only; the distillate was therefore saturated with carbonate of soda, to separate the body exerting the acid reaction, and frequently shaken during twenty-four hours, by which treatment the oily layer was diminished, and was separable by æther from the soda salts.

The acids which had not decomposed the carbonate of soda were extracted with æther, the æther separated by distillation, and the residue distilled with concentrated solution of potash, to remove the last traces of æther. Some of the above-mentioned indifferent oil was thus obtained, which it was extremely difficult to separate from the acid bodies. The remaining compound, consisting of this with potash, was then decomposed by bicarbonate of potash, and the product which passed over, amounting to about 25 grms., was dehydrated by long digestion with fused chloride of calcium, and lastly, rectified over the same.

The distillate was collected in five separate portions. Slight bubbling appeared at 248° F., oily drops and a milky fluid simultaneously passing over. The first portion contained so much water, that it soon separated into two layers; the second passed over between 338° and 356° F.; the third (the bulb of the thermometer only being surrounded with the hot vapour) between 356° and 383°; the fourth at 383°; and at the fifth the thermometer rose to nearly 392°; the portion distilling over then appeared somewhat brownish. The principal portion of the distillate was obtained between 356° and 383°, and consisted of a mixture of phenylic acid and water;

in none of the distillates could any difference be found from phenylic acid in odour, reaction with basic acetate of lead, perchloride of iron, and that with a shaving of deal. But in the last portions an important difference was found in the boiling-point, in the reaction with concentrated sulphuric acid, and lastly in the fact, that no crystallization could be produced by means of ice and common salt. Lastly, elementary analysis showed that the phenylic acid was mixed with a body which differed from it in containing more carbon and hydrogen.

The composition of phenylic acid being represented by the formula $C^{12} H^6 O^2$, that of the more highly carbonized body, which the author denominates *taurylic acid*, must be expressed by the formula $C^{14} H^8 O^2$.

Hence taurylic acid is isomeric with anisole, from which however it differs in its much higher boiling-point. This formula has also been assumed as that of creosote; but the author shows that it cannot be expressed by this formula, when Ettling's analyses, which are the only ones at present existing of creosote, are calculated according to the newer and more correct atomic weights. According to the author's view, Reichenbach's creosote is nothing more than impure phenylic acid.

As the taurylic acid could not be perfectly separated from the phenylic acid, its properties were not determinable; but important differences exist in its boiling-point being at least 18° F. higher; when strongly cooled, its not crystallizing; and in the circumstance, that when mixed with an equal volume of concentrated sulphuric acid, it forms a conjugate acid, sulpho-taurylic acid, which in a short time shoots into delicate white dendritic crystals, which gradually cohere into a spherical mass. The fourth portion of the distillate contained so much taurylic acid, that in a short time it solidified completely; the third however solidified only in part, and the portion which remained fluid consisted of sulpho-phenylic acid, as was proved by the analysis of the lead salt. Moreover, the ready conversion of the phenylic into nitro-picric acid placed its presence beyond any doubt.

The solution of the soda salts, which were separated from the phenylic and taurylic acids by treatment with æther, was evaporated to expel the æther, then decomposed with sulphuric acid and distilled.

The distillate, the odour of which was peculiar, somewhat resembling that of butyric acid, separated into two layers. The lower one formed a colourless heavy oily liquid, which amounted to about 4 grms.; the upper one was a solution of these acids in water, and strongly reddened litmus-paper. By boiling with carbonate of baryta, the acids were combined with this base, and the salts separated by crystallization. The salt which crystallized first contained a mean of 27·6 per cent. of baryta, and differed from the subsequent crystallizations, which gave a mean of 39·13 per cent. baryta, in the circumstance, that when heated, before undergoing decomposition it fused. The last crystallization was also fusible, and the amount of baryta exceeded 40 per cent. (41·0 and 44·64 per cent. were found).

The acid, the baryta salt of which contained 39·13 per cent. of baryta, was present in the largest quantity; the author proposes to denominate this *damaluric acid* (from δάμαλις and οὖρον), and that the baryta salt of which contained 27·6 per cent. of baryta, *damolic acid.*

The salts which last crystallized consisted of a mixture of damalurate of baryta with another barytic salt, in regard to which it remains still undecided whether the acid contained in it was butyric, valerianic, or another unknown acid. The solutions of all the barytic salts exerted an alkaline reaction; and the damaluric and damolic acids, when separated from the salts, were heavier than water.

On decomposing the damalurate of baryta with nitrate of silver, a silver salt was obtained. It formed a white powder, which did not become altered by exposure to light, and was but very slightly soluble in pure water. This silver salt was used to determine the elementary constituents of the acid and to control its atomic weight.

It was then found that the composition of the free acid must be expressed by the formula $C^{14}\,H^{11}\,O^3$, HO.

The composition of the silver salt is $C^{14}\,H^{11}\,O^3$, AgO, and that of the baryta salt $C^{14}\,H^{11}\,O^3$, BaO, which agrees perfectly with the amount of oxide of silver and baryta found in the salts.

Damaluric acid contains 2 equivs. less hydrogen than œnanthic acid, and bears the same relation to it as angelicic does to valerianic acid, and acrylic to propionic acid. Hence it appears that there is a second series of homologous acids, which differ from the so-called fatty acids in containing 2 equivs. of hydrogen less. Damaluric acid is best characterized by its barytic salt not fusing when heated, and after a red heat leaving a residue of carbonate of baryta, which retains exactly the shape of the salt.

Of damolic acid the atomic weight alone was determinable; this, when calculated from the mean of three determinations of the baryta, amounted to 2513·0. The atomic weight of coccinic acid is exactly the same (2562·5); but this acid, like the fatty acids coming nearest to it, is sufficiently distinguished by being solid at ordinary temperatures. Hence damolic acid may be supposed to hold the same position with regard to coccinic acid as damaluric does to œnanthic acid.

On comparison, no important difference was found between the urine of horses and cows; the volatile acids also existed in nearly equal quantities in the urine of both herbivora. That they occur in much less quantity in human urine has already been stated.

It still remained to be determined whether the above bodies pre-existed in the urine, or whether they were not resultants of the actions of the reagents used for separating them. 2500 grms. of cow's urine were therefore evaporated at a very gentle heat to one-eighth; when cold, mixed with dilute sulphuric acid; and, after standing for twelve hours, the hippuric acid separated by filtration. The deep brown mother-liquor was agitated with æther, the red ætherial solution drawn off with a siphon, and the æther evaporated. The residue was then treated with carbonate of soda, and the un-

combined acids extracted by æther. After the removal of the solvent, a reddish-brown semi-fluid mass remained, which, when distilled with a few drops of water, yielded heavy oily drops. These gave the reaction of phenylic acid with perchloride of iron, although its odour could not be distinctly detected; it was however perceived when the acids were combined with potash, the indifferent oil removed by distillation, and the residue decomposed with dilute sulphuric acid.

The soda salts were also decomposed with sulphuric acid, and the acids extracted with æther. The solution on evaporation left a dark brown residue, on the distillation of which with water, oily drops were obtained, which possessed the odour of the three acids described above, mixed with the well-known repugnant smell of cow's urine. Lastly, on simply distilling the urine, an ammoniacal product of a disagreeable odour was obtained, in which neither phenylic nor damaluric acid could be detected. It is thus evident beyond a doubt, that the acids in question are educts, and exist in the urine in combination with an alkali.

Lastly, if we reflect upon the origin of these acids, scarcely a doubt can be entertained that damaluric and damolic acids should be regarded as products of the transformation of animal substances, since similar volatile acids have been also found in the perspiration, in the various kinds of fats, and in the products of the oxidation of albumen, fibrine, caseine and gelatine.

The most unexpected result is the occurrence of phenylic acid and taurylic, which so closely resembles it, in the living body, especially as the former, according to the experiments of Wöhler and Frerichs, is decidedly poisonous. The author at first doubted the preexistence of this acid; the above experiment however leaves no doubt upon the point; it therefore merely remains for us to make some remarks upon its possible origin. As is well known, phenylic acid is readily formed from some members of the salicyle group, which appear to be pretty generally diffused through the vegetable kingdom. We may also admit that these compounds are transferred to the body in the food, and that the phenylic acid formed by their decomposition is immediately separated by the kidneys, and thus its injurious action prevented. Moreover, the observation made by Lehmann, that after the internal exhibition of salicine an extract is obtained by means of æther, from which water removes a body which is rendered blue by persalts of iron, appears to bear out this view, as the normal quantity of phenylic acid existing in the human urine is not sufficient to allow of its being detected in a small quantity of urine by this simple means.

This view is also especially supported by the fact, that Wöhler found both phenylic acid and salicine in castoreum, the source of which is evidently the food of the beaver, which principally lives upon the bark of the poplar and willow, hence substances abounding in salicine. Hence we may conclude that the urine of the beaver must contain a large quantity of phenylic acid; and as, according to E. H. Weber, the castor-bag is nothing more than sacciform

folded expansions of the *præputium penis* and *clitoridis* of the beaver, the construction of which permits of admission of the urine, there can be no doubt that the phenylic acid, salicine and benzoic acid, which occur in castoreum, are not formed in the bags, but are conveyed to them by the urine.

Hence castoreum consists of nothing more than the sebaceous secretion of the prepuce of the beaver mixed with the constituents of the urine; and its therapeutic action can scarcely be attributed to any other substance except the phenylic acid. But although the view that phenylic acid is derived from bodies belonging to the salicine group appears so well founded, yet the supposition that it originates from them only does not appear to be valid. Schlieper has found this acid, but in traces only, among the products of oxidation of gelatine; and as the change which organic matters undergo in the organism is in general exactly the same as that which ensues on decomposition by oxidizing matters, examples of which are presented in the metamorphoses of oil of bitter almonds and uric acid, it is also possible that phenylic acid may be formed, quite independently of external influences, from constituents of the body, among which the gelatinous tissues would hold the first place.

Lastly, as regards the formation of taurylic acid, what appears to be true in regard to the formation of phenylic acid, also holds good in regard to this. It is not improbable that it is derived from one of the benzoyle group of bodies, amygdalic acid. This compound is isomeric with anisic acid, and taurylic acid may also be formed from amygdalic acid in the same manner as anisole, which is isomeric with taurylic acid, from anisic acid.—*Nachr. der Gesellsch. der Wissensch. zu Göttingen*, 1850, p. 233.

On a new Cinchona Bark containing Quinoidine.

By Dr. F. L. Winckler.

Among some samples of barks recently received from London was one labelled *Bark from Maracaibo*. The author has examined this bark, and has obtained the remarkable result, that it contains kinovate of quinoidine in combination with a very peculiar yellow colouring substance, which produces no precipitate or alteration in perchloride of iron, and a considerable amount of quinate of lime, but only an exceedingly small quantity of quinotannine, and not a trace of quina-red.

The hot decoction of the bark obtained by treating 100 grs. with 4 oz. of distilled water, when strained hot, was perfectly clear, pale reddish-brown, and did not become turbid on cooling. It had an exceedingly disagreeable bitter taste, not at all like bark, and could be easily filtered. The filtered solution, on being tested with tannin, showed the presence of a considerable amount of alkaloid; perchloride of iron coloured the decoction slightly greenish-brown, without rendering it turbid; oxalic acid precipitated lime. The sulphate of copper gave no precipitate, although the bark contains a large quantity of kinovic acid. The author explains this by assuming that it

is too firmly combined with the colouring principle and the quinoidine. In the alcoholic extract of the bark, the decomposition of this substance is not even affected by lime.—Buchner's *Repert.*, vol. v. p. 194.

On Gregory's *Sulphuret of Nitrogen, and on the variety of Sulphur insoluble in Sulphuret of Carbon. By* MM. Fordos *and* Gelis.

In Graham's 'Manual of Chemistry' there is a compound described by the name of Gregory's sulphuret of nitrogen, which is said to be formed of 12 equivs. sulphur and 1 of nitrogen. We have attempted to reproduce this singular substance, but the results obtained have led us not to admit its existence. We nevertheless followed the directions of Dr. Gregory. We treated the chloride of sulphur with liquid ammonia; and after having observed all the peculiarities which accompany the reaction, and which have been described with the greatest care by M. Soubeiran, we obtained a yellow substance, possessing all the characters assigned by Dr. Gregory to the sulphuret of nitrogen, and especially that of furnishing an amethyst-red liquor when treated with alcohol containing a little potash. This coloration however quickly disappears.

As this property likewise belongs to a mixture of sulphuret of nitrogen and sulphur, it appeared probable that it was due to these two substances; and we had recourse to sulphuret of carbon to ascertain their presence. This liquid dissolved the greater portion of the mass. On evaporating the solution, it left a residue consisting of numerous octahedra of sulphur, coated with a small quantity of the ordinary sulphuret of nitrogen, and in some cases with traces of a golden yellow substance, sparingly soluble in sulphuret of carbon, and which proved to be a compound of chloride of sulphur with sulphuret of nitrogen. Whenever this happened, the residue required to be frequently treated with sulphuret of carbon in order to exhaust it; and the property of being coloured amethyst-red by an alcoholic solution of potash persisted for a long time; for the combination in question possesses this property, as well as the mixture of sulphur and sulphuret of nitrogen.

The residue insoluble in the sulphuret of carbon was dried, then reduced to powder and washed with hot distilled water, in order to remove a small quantity of muriate of ammonia which it still contained. We then found by analysis that it contained no nitrogen, water, hydrogen or chlorine; it then occurred to us that it might be an oxide of sulphur. To test the accuracy of this hypothesis, we treated a certain quantity of the substance with fuming nitric acid, in order to estimate the sulphur; the weight of the sulphate of baryta obtained showed that it consisted entirely of sulphur. But we have stated above that it was insoluble in sulphuret of carbon; it was therefore not ordinary, but a modified sulphur, analogous to the amorphous modification of phosphorus examined by M. Schrœtter.

M. Deville published in 1848, in connexion with several important observations on sulphur, the remarkable fact, that the sulphur

which has experienced sudden cooling, as in the flowers of sulphur and melted sulphur, leaves, when treated with sulphuret of carbon, an appreciable residue, varying from 0·11 to 0·35 of the primitive weight. It was evident that the insoluble sulphur which we had found in trying to prepare Dr. Gregory's sulphuret of nitrogen, was the sulphur discovered by M. Deville in the flowers of sulphur and the soft sulphur. M. Deville however attributes this modification of the sulphur to sudden cooling; but this explanation, which applied to the peculiar circumstances under which he observed it, cannot be admitted in the case we have described, as no heat was employed.

This production by the humid way of modified sulphur insoluble in sulphuret of carbon, led us to think it might be obtained under other circumstances; and we soon found that it occurs in very large quantity in the deposit produced by treating the chlorides of sulphur with water. This result clearly proves that in Dr. Gregory's experiment the ammonia merely gives rise to various compounds, which mix with the sulphur and alter its properties.

We have also met with this modification of sulphur in the deposit resulting from the action of hydrochloric acid upon solutions of the hyposulphates, and likewise in considerable quantity in the precipitate produced by the action of sulphurous upon hydrosulphuric acid in the presence of water. The sulphur obtained by treating the polysulphurets with acids contains but a trace. The crystallized native sulphur, that which is deposited by sulphureous springs, &c., and that arising from the slow oxidation of a solution of sulphuretted hydrogen, are, on the contrary, soluble without residue in sulphuret of carbon.

Whenever chemists have detected the production of different isomeric states of sulphur, they have always been obtained by the action of heat; and no one had previously indicated the possibility of the formation of one of these modifications under water.

The sulphur insoluble in sulphuret of carbon is likewise so in water, alcohol and æther; it may be boiled in distilled water for a long time without losing its property. When heated in an oil-bath to about 220° in a glass tube in which has been placed for comparison a piece of ordinary sulphur, it remains solid for some time after the ordinary sulphur has melted; but if the temperature be maintained between 220° and 248°, it is gradually modified, and fuses, and now dissolves without residue in sulphuret of carbon.—*Comptes Rendus*, March 17, 1851.

On Bromobenzoic Acid. *By* M. Peligot.

M. Müller has recently asserted that the production of bromobenzoic acid is opposed to certain theories of M. Laurent. At the request of the latter chemist, M. Peligot has made a fresh examination of this acid; whence it follows, that, in accordance with the theories of M. Laurent, it is not bibasic, and its silver salt is $C^{14}(H^4 Br, Ag)O^4$.—*Comptes Rendus*, xxxi. p. 11.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

April 7, 1851. (Dr. Daubeny, President, in the Chair.) The following papers were read:—

"On the Composition of the Waters of the Dee and Don at Aberdeen, with an investigation into the action of Dee Water on Lead Pipes and Cisterns." By John Smith, M.D., Fordyce Lecturer on Agriculture, and Assistant in the Chemical Laboratory of Marischal College.

The subject of this paper is discussed under the following heads:—

1. *General Characters of the Districts drained by the Rivers Dee and Don.*—The sources of the Dee lie amidst lofty granite mountains. The length of country traversed by it is about eighty miles, or sixty-five miles in a straight line, and the extent of country which it drains about nine hundred square miles. Its banks are gravelly, its flow pretty rapid, and the alluvial deposits few and of limited extent. From the small proportion of clay and peat in its course, its waters are usually quite clear.

The water for the supply of Aberdeen is taken from the Dee about two miles from its mouth, and quite beyond the reach of the tide-water. It percolates through the gravelly sides and bottom of the river into drains, and is there pumped to the highest level of the town. It is distributed through iron mains, and taken into the houses by small lead pipes, to which lead cisterns, generally of small dimensions, are commonly attached. The supply is constant, and amounts to about one million gallons per day.

The sources of the Don lie immediately north of the districts drained by the Dee, and comprise a less extensive area, including mossy ground, encircled by granite hills. Its course is about sixty miles in length to Aberdeen, or about forty-five miles in a straight line. The mountains among which it runs contain more limestone than is found in those about the Dee. Hence the waters of the Don contain more lime, and are more coloured by peat than those of the Dee.

2. *Composition of Dee Water.*—A specimen taken some miles up the river, on the 24th of September 1850, three days after heavy rain, was found to contain in the gallon, 4 grs. of solid matter, consisting of—

	grs.
Carbonate of lime	0·850
Sulphate of lime	0·121
Sulphate of magnesia	0·323
Chlorides of potassium and sodium	0·670
Phosphates of lime and iron	0·080
Silica	0·140
Organic matter and loss	1·816

This specimen had a brownish tint, whereas the Dee water is generally colourless, and in other respects it was less pure than

usual. A second specimen, taken when the river was in its usual clear and transparent state, yielded 3 grs. of solid matter from the gallon, of which only 0·4 of a grain was organic matter, or volatilized by heat.

3. *Composition of Don Water.*—Two specimens of this water were examined, one taken about a mile from the mouth of the river, and the other about thirty-five miles higher up. The former was found to contain 8·65 grs. of solid matter in the gallon, of which 3 grs. consisted of organic matter; the latter contained 5 grs. of solid matter in the gallon, of which 1·2 gr. was organic. The composition of the solid contents of a gallon of the first specimen is thus represented:—

	grs.
Carbonate of lime	2·18
Sulphate of lime	0·17
Sulphate of magnesia	1·00
Chlorides of potassium and sodium	1·32
Phosphates of lime and iron	0·38
Silica	0·60
Organic matter	3·00

4. *Action of Dee Water on Lead.*—About forty trials were made with the view of ascertaining the action of Dee water on the pipes through which it is conveyed to the houses. These pipes vary from 12 to 100 yards in length. In some instances no indications of the presence of lead, in the water which had passed through the pipes, were found; in others, however, small quantities of lead were detected in solution. The quantities varied from less than $\frac{1}{100}$th of a grain to about $\frac{1}{20}$th of a grain of lead in a gallon of the water.

From an inquiry into the influence of the use of this water upon the health of the inhabitants of Aberdeen, in connexion with what has been observed elsewhere, the author concludes that less than $\frac{1}{20}$th of a grain of lead in the gallon of water produces no deleterious effect upon the health of those using the water for dietetical purposes, and that the limit of the deleterious action is between $\frac{1}{10}$th and $\frac{1}{20}$th of a grain of lead to the gallon of water.

"On a Peculiar Property of Æther and some Essential Oils. By Dr. C. F. Schœnbein.

The property referred to by the author is similar to that which phosphorus has been long known to possess, when put, under certain circumstances, in contact with pure oxygen, or with atmospheric air, of developing a highly oxidizing agent, which has been called ozone.

The author finds that if a little pure æther be put into a bottle filled with pure oxygen or atmospheric air, and exposed to diffused light, the bottle being occasionally shaken, the æther, after the lapse of four months, will have acquired new properties. Although producing no action upon blue litmus paper, it will discharge the colour of solution of indigo, convert pure phosphorus, when immersed in it, into phosphorous acid, eliminate iodine from iodide of potassium,

change pure sulphate of protoxide of iron to the basic and acid sulphates of the deutoxide, transform yellow prussiate of potash into the red salt, convert sulphuret of lead into the sulphate, &c.

Similar effects are produced with oil of turpentine and oil of lemons, when treated in the same way as the æther.

The author expresses an opinion that the property which these substances thus acquire, is due to the presence of oxygen in a chemically exalted condition.

Royal Society.

June 13, 1850. (The Earl of Rosse, President, in the Chair.) The following papers were read:—

"On the Variations of the Sulphates and Phosphates in the Urine in Disease." By Henry Bence Jones, M.D., F.R.S.

The object of the paper is to show whether the sulphates in the urine are increased or diminished in any class of diseases. The corresponding variations of the phosphates were determined. The conclusions may be thus stated:—

1. In three cases of acute chorea the most remarkable increase was observed in the amount of sulphates in the urine. In the same cases the quantity of urea was very much increased. The quantity of urine made in twenty-four hours was not excessively diminished, and the total amount of earthy and alkaline phosphates was below the average amount, sometimes remarkably less than in health.

2. In delirium tremens and in other delirium a remarkable increase in the amount of sulphates in the urine was frequently observed, and the total amount of phosphates was in the same cases occasionally remarkably diminished; and the resemblance to the state of chorea was still closer, inasmuch as occasionally a very great excess of urea was found in these cases also.

3. In acute inflammatory affections of the nervous structures, during the most febrile symptoms, an increase was observed in the amount of sulphates in the urine; and the total amount of earthy and alkaline phosphates in these diseases was increased in the same proportion as the sulphates were increased.

4. In some slight and chronic diseases of the nervous structures no increase in the amount of sulphates in the urine was observed, excepting when sulphate of magnesia had been taken.

5. In acute diseases, in which neither the nervous nor the muscular structures were chiefly affected, no increase in the sulphates or phosphates was observed, except after sulphate of magnesia.

6. In chronic diseases, in which neither the nervous nor the muscular structures were chiefly affected, no decided increase in the sulphates or phosphates in the urine was observed, except after sulphate of magnesia. One case of substosis may be regarded as a doubtful exception to this statement.

The general conclusions are—

That in acute chorea, in which the muscles are in excessive action, the sulphates and urea in the urine are greatly increased.

That in delirium tremens the same state of urine is frequently met with when the phosphates are not at all increased.

That in acute inflammation of the nervous structures sulphates and phosphates are both increased in the urine.

That in chronic diseases of the brain, and in other acute and chronic inflammations, no increase of the sulphates is observed except after sulphate of magnesia.

The result is that muscular action increases the sulphates in the urine without increasing the phosphates; and that inflammation of the brain increases the sulphates as well as phosphates in the urine.

"Second Appendix to a paper on the Variations of the Acidity of the Urine in Health." By Henry Bence Jones, M.D., F.R.S.

In a previous paper and appendix, the effect of different diets, of sulphuric and tartaric acids, of caustic potash and tartrate of potash on the acidity of the urine was traced. In this appendix tartrate and carbonate of ammonia are the substances whose influence is determined, the object being to examine the comparative effect of fixed and volatile alkalies.

The first day two drachms of tartrate of ammonia were taken in distilled water, the second day 288 grains were taken, and the third day 177 grains.

Comparative experiments were made when no tartrate of ammonia was taken; the result was that tartrate of ammonia caused no perceptible diminution of the acidity of the urine. The difference between tartrate of ammonia and tartrate of potash may be shortly stated thus: two drachms of tartrate of potash made the urine alkaline in thirty-five minutes after it was taken, whilst three drachms of tartrate of ammonia produced no perceptible effect on the acidity of the urine.

The sesquicarbonate of pharmacy was then tried. The first day 18 grains were taken dissolved in distilled water, the second day 40 grains, the third day 80 grains. Comparative experiments were made without the volatile alkali, and it was found that in these doses carbonate of ammonia did not diminish the acidity of the urine; on the contrary, the acidity was higher than usual, and it was increased for twenty-four hours after the volatile alkali was taken.

Further experiments were made with 80 grains of carbonate of ammonia on two different days: no diminution of the acidity of the urine was produced on either day. The first day the quantity of urine was much increased, and thus probably an increase in the acidity of the urine was not evident. The second day on which the carbonate of ammonia was taken the increase in the acidity of the urine was perceptible.

Thus the effect of volatile alkali on the acidity of the urine is totally distinct from the effect of fixed alkali; and the author considers, that by determining the variations of the nitrates in the urine, the cause of this difference will be discovered.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Nitrite of the Oxide of Æthyle. *By* Dr. A. STRECKER.

THE composition of the so-called nitric æther has been established by the analysis of Dumas and Bonnet, who arrived at the empirical formula $C^4 H^5 NO^4$. Chemists differ in opinion as to the rational composition, the majority having adopted the view that the so-called nitric æther belongs to the compound æthers, and must consequently be considered as a combination of anhydrous nitrous acid with oxide of æthyle, $C^4 H^5 O, NO^3$, or as the hydrate of nitrous acid in which 1 equiv. hydrogen is replaced by 1 equiv. æthyle, whilst other chemists do not reckon it in this class of compounds. Of the most recent views I shall notice only that of Gerhardt, who considers the so-called nitric æther as the nitro-compound of the hydrocarbon $C^4 H^6$ (acetene), and writes its formula accordingly, $C^4 \begin{matrix} H^5 \\ NO^4 \end{matrix}$.

The most decisive character of an æther is its separation into alcohol and an acid by the action of alkalies. Now according to Liebig's statement, this nitric æther is resolved, on treatment with hydrate of potash, into alcohol and nitrite of potash. No difference of opinion could therefore exist as to the constitution of this body, if this mode of decomposition, which was only proved by qualitative reactions, had not been brought into doubt; I have therefore been induced to make some experiments on the decomposition of nitric æther by potash.

The nitric æther used in the following experiments was disengaged according to the method of E. Kopp, by mixing alcohol, nitric acid and copper shavings together; freeing it from any admixture of nitric oxide or nitrous acid, by passing it through a lukewarm solution of protosulphate of iron in water, and condensing it in a freezing mixture. The slightly-yellowish mixture thus obtained was decomposed in closed vessels with fragments of hydrate of potash; at first it turned quite brown, indicating the presence of aldehyde in the nitric æther prepared according to the above method; and a crystalline salt separated, which disengaged copious red fumes upon the addition of sulphuric acid. The separation of this crystalline salt continued for several days, that which fell last being least coloured. After standing for several days, the liquid was mixed with water, any still-undecomposed nitric æther expelled by a gentle heat, and the residual

liquid submitted to distillation; the product exhibited the properties of dilute alcohol.

The so-called nitric æther was decomposed far more readily by an alcoholic solution of hydrate of potash than by pieces of hydrate of potash; in this case the liquid also turned brown, and the salt which first separated was of a dark colour. The yellowish-brown liquid decanted from the latter gradually deposited, on being set aside, more crystals, which, after pressure between blotting-paper, proved to be pure nitrite of potash. Its aqueous solution was precipitated with nitrate of silver, the precipitate dissolved in boiling water, whence it crystallized on cooling in slender needles. 0·2036 grm. of these crystals, dried in the air, left on calcination 0·1428 grm. or 70·1 per cent. of silver. The nitrite of silver, AgO, NO^3, contains according to theory 70·1 per cent. of silver.

There can therefore no longer be any doubt that the so-called nitric æther yields, on decomposition with alkalies, alcohol and alkaline nitrite, and consequently belongs to the class of compound æthers; it is certainly decomposed with some difficulty by hydrate of potash at the ordinary temperature; but, as is well known, the æthers differ very much with respect to their facility of decomposition. The affinity of the nitrous acid for the oxide of æthyle is exceedingly great, as the easy formation of the nitrite of the oxide of æthyle shows.—Liebig's *Annalen*, March 1851.

Analyses of Two Specimens of Bronzes of the Gallo-Roman Period. By M. Salvetat.

Although numerous analyses of ancient metallic alloys have been already published, it still appears useful that the composition of these two antique bronzes, found in a tomb in the celebrated City of Lime, should be made known, as researches of this kind have an incontestable value for the industrial arts; and beyond this and the general interest they possess, they serve to give some idea of the state of chemical knowledge among the ancients.

It is much to be regretted, that all analyses of a similar description to those which form the subject of this memoir have not been accompanied by sufficiently precise details with respect to the circumstances which led to the discovery of the alloy analysed, and the epoch to which it was supposed to belong. These details would certainly throw considerable light upon ancient metallurgy; for although it is true that the application of the principles of art is well shown in most subjects of ancient origin, without a knowledge of their period, our positive knowledge of the processes practised by the ancients in different ages of antiquity can receive but little addition. Much time will yet doubtless pass away before this question will be materially elucidated; in the meantime, no opportunity should be lost of entering into investigations connected with the chemical part of the subject. It seldom happens that antiquaries are willing, from the love of another branch of science, to sacrifice the whole or part of that which chance has thrown into their hands, or which has cost

them lengthened search, expense and pains. The author of this paper was so fortunate as to have an opportunity afforded him by M. Feret of Dieppe, of examining the chemical composition of two bronze rings, which he had himself found under circumstances of the whole of which he has preserved a particular account. In it he describes the locality whence the rings were obtained, and the people and period to which they are supposed to have belonged.

One of these rings was, externally blackish, fragile, and with a grayish fracture; it was about $13\frac{1}{2}$ millims. in external diameter, and was found in a state of complete preservation. Its composition was as follows:—

Tin	23·52
Copper	75·55
Lead	0·47
Loss	0·46

with traces of silver, nickel and antimony, but no zinc.

The other ring was less fragile than the first, and its fracture was slightly yellow. Its exterior was not of so dark a colour, and its diameter externally was $22\frac{1}{2}$ millims. It showed here and there points of alteration, in which carbonate of copper was formed, of a green colour. The composition of this ring was—

Tin	15·73
Copper	79·93
Lead	3·50
Loss	0·84

with traces of silver, without nickel or zinc.

Both these rings were found in the same tomb. The following is an extract from a letter of M. Feret, in which he enters into the subject of the supposed origin of these bronzes:—

"I found these rings in 1826, among others of the same kind, in a Gallo-Roman tomb, which, according to appearances, dated from the latter half of the fourth century.

"Among the medals scattered about in the same monument, the latest in date was of the time of Fl. Valens, who died in 378. The pottery found near the skeleton, which the tomb enclosed, belonged, judging from its character, to the same epoch.

"It should however be remarked, that this tomb was situated in the City of Lime, a vast enclosure, surrounded by entrenchments about a league to the north-east of Dieppe; and that in the soil of this enclosed space are found the remains of several periods of antiquity, differing much from one another. The epoch, purely Gallic, is frequently shown by its remains; and in the inferior strata of the soil of this tomb are discovered pottery, hatchets and medals, supposed to be Celtic. I believe however that the rings now analysed belong to the fourth century, as they resemble other objects of the same nature, which I have been able to class with other Gallo-Roman antiquities."

The absence of zinc in the compounds or alloys described above is not surprising. M. Gœbel announced long ago, both from his

own researches and those of Vauquelin and Klaproth, that the bronzes of ancient Greece and her colonies, no matter whether found in Greece, Italy, Egypt or Asia Minor, are all composed essentially of lead, copper and tin, or simply of copper and tin. The analyses of ancient Grecian medals, performed in the laboratory of M. Erdmann, also confirm this opinion. The analyses of M. Fresenius, of M. Knapp, made upon Celtic bronze weapons, those of M. Moëssard of ancient bronzes, found in the department of the Oise, belonging to the Roman period, and lastly those described in the present paper, tend to generalize the fact stated by M. Gœbel, and to extend it to the Celtic, Gallo-Roman and Roman epochs.

The presence of nickel in one of the rings taken from the tomb of the City of Lime is not an isolated circumstance. M. Fresenius also detected its presence in a Celtic hatchet found near Giessen; and M. Knapp has likewise found it in a Celtic hatchet, which was buried in a peat-bog near Ceriguey-Druydon, in Wales.

The excellent preservation of the rings described above is probably attributable to the large proportion of tin which enters into the composition of the alloy of which they are made.—*Ann. de Chim. et de Phys.*; and Newton's *Journal*, April 1851.

Observations on the Urine in Pneumonia. By Dr. Redtenbacher.

The author was engaged in the year 1846 in making a series of experiments on the urine of patients labouring under different acute and chronic diseases, with the view of determining,—first, the relation which subsists between the presence of inorganic salts and the specific gravity of the urine; and secondly, whether the increased or diminished proportion of these saline constituents is connected with the formation or retrocession of certain morbid processes. His observations were made in Skoda's wards in the Great General Hospital of Vienna. He found that the amount of inorganic salts was not subject to much variation, and consequently affected the density of the urine in a very trifling degree; but that its density depends upon the organic compounds, and especially upon the urea and uric acid. In cases of pneumonia, he has satisfied himself that the amount of chlorides in the urine undergoes variations dependent upon the stage of the disease. Healthy urine, as is well known, deposits a copious precipitate on the addition of nitrate of silver. Redtenbacher asserts that in all the cases of pneumonia (amounting to 80) in which he has applied this test, the faintness or absence of the precipitation has indicated a diminution or absence of chlorides. The precipitate becomes less distinct, from day to day, till resolution commences, when the chlorides again gradually resume their normal proportion. Diminution of the chlorides likewise occurs in typhoid fever, in acute arthritis, and in capillary bronchitis; but is neither a constant phænomenon in these diseases, nor observed at any certain period of the morbid processes. In cases of tubercular infiltration, chlorides are found in the urine in normal proportion, but suffer diminution for a short time during each fresh infiltration.

Redtenbacher anticipates the objection as to the value of these observations, that the amount of the chlorides of the urine depends upon the amount of culinary salt used with the food, and that the quantity of the former will be diminished with the supply of the latter,—first, by showing that the chlorides are not equally diminished in the course of other diseases in which restricted diet is rigidly enforced; and secondly, by mentioning that Skoda's cases of pneumonia, on which his observations were made, were, from beginning to end of the disease, allowed a drink acidulated with muriatic acid. He believes, consequently, that the uniform diminution of chlorides in the urine of pneumonia is somehow essentially connected with the morbid process.—*Zeitschrift der k. k. Gesellschaft der Aerzte zu Wien*, August 1850; and *Edinb. Monthly Medical Journ.*

√ *Researches on Cobalt. By* E. Fremy.

Chemists are aware that certain metallic oxides are capable of uniting with ammonia to form new bases, in which the properties of the oxides and of the ammonia are completely masked. The bases which result from the action of ammonia on the protochloride of platinum present an interesting example of these ammoniacal compounds. The present investigation has for its object to show that the oxides of cobalt, more highly oxidized than the protoxide, can combine with ammonia and form several new series of salts, having as base, ammonia, oxygen and cobalt.

The mode of production of these compounds will be easily understood. When a salt of cobalt is acted upon by ammonia, the liquid does not become coloured when preserved from contact with the air; but as soon as it is exposed to the influence of oxygen, it immediately acquires a brown colour, absorbs this gas with rapidity, and frequently deposits crystals, which are remarkable for their regularity. The salts which are produced in this reaction have for base ammonia combined with the oxides of cobalt. As cobalt combines with oxygen in several proportions, the same salt, submitted to the action of ammonia and oxygen, is able to produce several saline compounds containing ammonia combined with cobalt at different stages of oxidation; thus the nitrate of cobalt, rendered ammoniacal and then exposed to the influence of the atmosphere, deposits successively three crystalline salts differing in their properties, and in which the proportion of oxygen is successively increased.

These new salts frequently exhibit very remarkable properties; thus the first compound, which crystallizes when the ammoniacal nitrate of cobalt is oxidized by exposure to the air, is decomposed with effervescence in cold water, with disengagement of pure oxygen.

The study of the products resulting from the decomposition of the salts of cobalt, whose mode of formation I have just described, is highly interesting; for on submitting the salts which contain most oxygen either to the action of boiling water or to the influence of dilute acids, they are deprived of a portion of the oxygen which they had absorbed in the presence of the ammonia; and in this

manner perfectly crystalline salts, having for base the intermediate oxides of cobalt, are produced, in the examination of which I am at present engaged.—*Comptes Rendus*, April 7, 1851.

On the different Chemical Conditions of the Water at the surface of the Ocean and at the bottom, on Soundings. By Aug. A. Hayes, *Assayer to the State of Massachusetts.*

Considering the surface which the ocean covers in comparison with any large extent of land surface, we might be led to expect a want of uniformity in the distribution of saline matter throughout its mass. Those parts reposing in immediate contact with saline deposits and many decomposing rocks, would every instant receive more soluble matters than contiguous portions; and while matter to be dissolved remained, the balance of distribution would be disturbed. Local differences are known to exist, and are referred to the influence of evaporation, and to lower and upper currents, with great degree of probability. Still the belief that the water of the ocean has existed during the lapse of great geological periods of time, with the same or even a large proportion of saline matter, must gradually give way as facts connected with the decomposition of rocks are attentively studied.

The phænomena which form the subject of this communication are only remotely connected with this point of unequal distribution, being related to *kind* rather than quantity of saline parts.

The mass of ocean, exposed on its surface to the mixture of gases forming our atmosphere, absorbs both constituents, the oxygen in the larger proportion. Winds greatly favour this effect, and the increased quantity found in the water after storms is referred to this action.

When ocean water, taken at the same moment from the surface and only 100 to 200 feet under this surface, is subjected to the usual course of analysis, a larger proportion of oxygen is constantly found in the surface samples. Trials made at points from the temperate to and within the torrid zone corresponded, and only slight deviations were found in the moving water of the Gulf Stream. Another kind of evidence of this fact is afforded by the observations made on the corrosion of the copper sheathing of vessels. Slight inequalities in the kinds of copper used exist; but when a large number of cases are included and the time of observation is considerable, this influence is hardly seen. It is a general law that copper sheathing corrodes most rapidly at those parts of the covered surface where by agitation the most air is dissolved in the water passing in contact with it. The fact is well known, that sea-water deprived of air has no action on copper even after many years' exposure; and this relation becomes changed when we allow the same water to dissolve air. Some persons, who have noticed this uniformity of corrosion at the points where the water contains the most dissolved air, have attempted an explanation on mechanical principles. They have assumed that greater friction between the moving surface and the

water takes place at those points. It is not uncommon for vessels to make long voyages and return with the *chalked numbers of the sheets legible*, and active corrosion *seldom* takes place on those parts of the coppered surface really exposed to the greatest friction.

If we assume that the oxygen of sea-water is almost wholly derived from solution of one part of the atmosphere, then the surface under existing conditions should contain the largest amount. The organized beings of the ocean, consuming the oxygen as diffused, would constantly diminish the quantity below, and allow an inequality to exist.

The reactions taking place in the corrosion of copper by the surface-water of the ocean, considered in all their particulars, become quite complex. Without entering minutely into these, it is sufficient to adopt the usual expression, that the oxidation and corrosion of copper take place in consequence of the decomposition of hydrochlorates under the presence of oxygen and metal, a very common change, resulting in the production of oxides and chlorides.

While pursuing the subject of copper corrosion at the surface, I was some years since led to examine samples of copper which had remained some time at the bottom of the ocean. In these cases an opposite kind of action was at once recognised; and the observations have been so far multiplied, that I think a constancy of result will be observed in all cases on soundings.

Copper and bronze, and even a brass compound, were found thickly incrusted with a sulphuret of copper, formed often in crystallized layers, having a constant chemical composition, entirely free from chlorine or oxygen, the corroding agents of the surface. Specimens of copper and bronze from mud and clay at different depths, and in one instance from clean sand below a powerful rapid, have given thick layers of sulphurets of copper, or copper and tin.

These observations have been lately extended, and as they include other materials, I shall state them more particularly.

The Spanish vessel San Pedro de Alcantaro was blown up off the coast of Cumana in the year 1815, and a large amount of specie dispersed and sunk. A large part of the silver dollars has been recovered during the past year, by our enterprising countrymen, from a depth between 50 and 80 feet. The coin reposed in mud, and was sometimes covered by a stratum of coral from 6 to 12 inches thick.

Two pieces of the coinage of 1810 and 1812 were taken for analysis. The weight of such dollars, slightly worn, was 412 grs. nearly. When the coin of 1810 had lost its covering, it weighed 330 grs., or 82 grs. of the substance of the dollar had assumed the state of a sulphuret. The other weighed 356·82, or less by 55·18 grs. By exposure during thirty-five years in one case, 100 parts of the coin had been destroyed to the extent of nearly 20 parts, the other 13·39, giving an average of 16·52.

These incrustations were crystallized distinctly, and their composition was carefully determined. Water abstracted traces of chlo-

rides of sodium and magnesia with sulphate of lime only. Acetic acid took up a compound of chlorine, carbonate of lime and oxide of copper in minute quantity. The investing coating was removed from one coin by making it the negative pole of a single galvanic circle in dilute sulphuric acid, so as to obtain the covering in sheets, a loss of sulphur taking place. Water acidulated with nitric acid, after several days, detached the covering from the other; and this sample was used for determining the sulphur, in the form of sulphuric acid, as well as the bases. Operating in this way, it was found that very small portions of chlorides of sodium, magnesium and sulphate and carbonate of lime adhered to the incrustation, while the pure portion of this consisted of bisulphuret of copper with sulphuret of silver and gold; even the minute trace of the latter metal in the silver being mineralized by sulphur.

Connected with this observation is another I have made on the corrosion of an alloy of 1 silver in 500 copper, used as sheathing, in which both metals united to chlorine and oxygen, and were removed rapidly and largely by surface-water, as a simple metal would have been.

No opportunity has yet offered for continuing these examinations on copper and other metals obtained from great depths of water; and in calling the attention of chemists to this action, I hope to obtain results from those who are more favourably situated for observation.

The opposite tendencies of the two parts of the ocean on soundings being shown, a large mass, distinguished as "green water," is really placed as it were between the poles of a gigantic single galvanic circle; and we are thus enabled to explain many anomalous decompositions taking place within such limits.

In looking for the cause of the transfer of sulphur from its oxidized state, in saline compounds, to the metals on the bottom of the ocean, I have concluded that the waters from the land exert a most important influence. These waters are never destitute of organic matter in a changing state. This matter, dissolved from the surface of the earth or from rocks in percolating the strata, assumes a state in which it powerfully attracts oxygen. Waters holding this matter in solution readily decompose sulphates of lime and soda, even when partially exposed to atmospheric air. The line at which the saline waters of the ocean and the under-land flow of water meet is the place where observations have shown that the greatest chemical action exists. Ordinary decompositions of sulphates by organic matter in ocean water are hardly known to take place. The phænomena at once become distinct when land-waters are allowed to mix, and the water from deep wells in the vicinity of the ocean has a more highly marked chemical action than rain-water. The decomposition of the sulphates proceeds under the presence of carbonic acid, and carbonates of the alkaline earths are products of the change.—Silliman's *Journal*, March 1851.

Observations on Phosphorus. *By* Prof. A. Schrœtter.

The *red phosphorus* is phosphorus in an allotropic condition, which stands in the same relation to the ordinary crystallized modification as charcoal to the diamond. Oxygen has no influence on its formation, for it is also produced in gases perfectly free from oxygen. The conditions requisite to convert the crystallized into amorphous phosphorus are light and heat; both act in a perfectly similar manner; the one assists the action of the other. At 419° F. phosphorus slowly passes into the red modification, more quickly between 464° and 482°, and still more so when at the same time light shines upon it. The red phosphorus is much harder than the crystallized; and when it is broken at 32° F., there is evolution of light, and it takes fire. This metamorphosis of the phosphorus may be effected in atmospheres of hydrogen, carbonic acid and nitrogen. After being heated for the above temperature, it continued for a long time (thirty-six days) liquid even at 23° F., and then solidified in diffused light into red phosphorus. The experiments were made in retorts or glass tubes, or bulb-tubes, from which the air had been previously expelled by other gases or the oxygen had been consumed.

The red amorphous phosphorus may be separated from any admixture of the white kind by sulphuret of carbon, in which it is insoluble. When completely washed by sulphuret of carbon, it forms an amorphous powder without the least lustre, the colour of which varies from a scarlet to a dark crimson, or even dark brown and brownish-black. When the powder is covered by a liquid, the colour increases considerably in brilliancy; but when rubbed upon paper, it has a dead brownish-red colour. Each time, on heating it, the colour appears a dark violet. The specific gravity of amorphous phosphorus is 1·964 at about 50°. It is perfectly unalterable in the air, and insoluble in sulphuret of carbon, alcohol, æther, naphtha and protochloride of phosphorus; oil of turpentine, and indeed all bodies which boil at a high temperature, take up a little during ebullition; but no substance has hitherto been found which dissolves it on the application of heat, and again deposits it unaltered, *i. e.* in the amorphous state, on cooling.

When amorphous phosphorus is heated in a bulb-tube placed in an oil-bath, after all atmospheric air has been previously expelled by dry carbonic acid, it begins to change into the ordinary phosphorus at 500°; if, while it is being heated, air is passed through the apparatus, it takes fire nearly at about the temperature at which it passes into ordinary phosphorus. With the use of oxygen, ignition likewise results at about 500°, and the temperature must even be raised to 572° for the combustion to be perfect, as a portion of it is protected from the action of the oxygen by the phosphoric acid which is formed. Amorphous phosphorus does not light in the least at the ordinary temperature, but it begins to show a feeble light at the temperature near which it takes fire. But if it is allowed to cool after it has once begun to light, it each time ceases. Chlorine gas acts upon amorphous phosphorus at the ordinary tempera-

ture, and then gives, with evolution of heat but without any appearance of light (which is very remarkable), protochloride of phosphorus, and then perchloride. Solution of caustic potash dissolves amorphous phosphorus on boiling, with evolution of non-inflammable phosphuretted hydrogen, the more readily the more concentrated the solution. In this operation the finely-divided amorphous phosphorus experiences a very remarkable change of colour; it turns of such a dark chocolate-brown as to appear nearly black. This change occurs with very concentrated ley, even at the ordinary temperature, in the course of twenty-four hours; but with a dilute solution of potash, long ebullition is requisite; this change likewise takes place less readily the less finely divided the phosphorus. When the nearly black amorphous phosphorus thus obtained, which however does not essentially differ from the red modification, is mixed with ordinary fused phosphorus, black sticks of phosphorus may be obtained. From its further behaviour towards iodine, nitric acid and other substances, it is evident that it is,—1st, on the whole far more indifferent than the ordinary phosphorus; 2nd, that it is insoluble; 3rd, that it possesses the property of combining with other bodies, with evolution of light, in a far less degree; and lastly, 4th, that it deprives very many oxygen compounds of their oxygen, with the appearance of flame, on the application of heat, by friction or percussion.

Schrœtter has recently prepared the red phosphorus in coherent masses; and he expects, from its being much less dangerous than the ordinary phosphorus, that it will become an article of commerce. It is prepared by keeping the ordinary kind for eight days as nearly as possible at the temperature at which the red again passes into the usual modification. It is then converted into a perfectly coherent reddish-brown mass, exhibiting perfect metallic lustre and an iron-black fracture. It is brittle, very fragile, with a perfect conchoidal fracture, the fragments being irregular with sharp edges. The streak of this mass exhibits exactly the red colour of the powder, so that in this respect the similarity in the natural history properties with a variety of rhomboidal iron ore, blood-stone, is almost complete. The hardness of the coherent amorphous phosphorus is very considerable, viz. 3·5, and consequently intermediate between that of calcareous spar and fluor spar. Its specific gravity is 2·089 at 63°, which is exactly the number which Böttger found for the ordinary kind; this coincidence is accidental, as it still contained 0·2–0·3 per cent. of the ordinary modification. Moreover, some pieces of amorphous phosphorus, which had been exposed for a long time to the action of heat and contained much less of the ordinary modification, had a specific gravity of 2·106.

In observing the properties of the red phosphorus, it is especially necessary to guard against any admixture of the ordinary kind; the spontaneous ignition on breaking a stick of amorphous phosphorus, and the phosphorescence in the dark, is owing to this admixture, and not to the red modification itself.—Poggendorff's *Annalen*, lxxxi. p. 276.

On some Salts of Arsenic Acid. *By* M. Kotschoubey.

The author has examined the combinations of arsenic acid with the alkalies and alkaline earths. For estimating the arsenic acid, he employed an exactly similar method to that described by Raewsky for the quantitative determination of phosphoric acid.

The salts $2KO, HO, AsO^5$ and $2NaO, HO, AsO^5$ were obtained by saturating arsenic acid with the corresponding carbonates. According to the author, the soda salt crystallizes with 26 equivs. water of crystallization. This is opposed to the statements of Mitscherlich, who found in it 24 equivs., the same as in the ordinary phosphate of soda. $2KO, HO\ AsO^5$ is deliquescent, and does not crystallize. It melts, like the soda salt, at a tolerably high temperature, without being decomposed.

To prepare the salts $3KO, AsO^5$ and $3NaO, AsO^5$, arsenic acid is fused with an excess of nitrate of potash or soda. With respect to the acid salts, the author's analyses confirm the composition assigned to them by Mitscherlich. The following double salts were obtained by mixing the neutral salts:—

$$KO, NaO, HO, AsO^5 + 18HO$$
$$Na, AmO, HO, AsO^5 + 8HO$$
$$KO, AmO, HO, AsO^5 + xHO$$

Mitscherlich found in the arseniate of potash and soda 16 equivs. water.

By carefully heating the ammonia double salts, the author thinks he obtained an arsenic acid analogous to the metaphosphoric acid; but its quick conversion into the tribasic modification did not allow of closer examination.

The combinations of arsenic acid with the alkaline earths were found to correspond exactly with the phosphoric acid compounds analysed by Raewsky. $2CaO, HO, AsO^5 + 3HO$ is obtained as a crystalline precipitate when a solution of neutral arseniate of soda is poured by drops into a solution of chloride of calcium. $2CaO, HO, AsO^5 + 2HO$ is obtained when, on the contrary, a solution of chloride of calcium is poured into the arseniate of soda. The salt $3CaO, AsO^5 + 3HO$ is formed when the precipitation is made with the addition of ammonia.

By supersaturating a solution of the neutral lime salt $2CaO, HO, AsO^5$ in muriatic acid with ammonia, a salt was obtained with the formula $2CaO, AmO, AsO^5 + 12HO$, corresponding to the arseniate of ammonia and magnesia. By mixing chloride of calcium with an excess of arseniate of soda, a salt was obtained with the formula $6CaO, AsO^5 + 6HO$, which at 248° parted with the whole of its water, leaving the anhydrous compound $6CaO, AsO^5$.

By precipitating a hot solution of arseniate of soda with chloride of strontium and chloride of barium, crystalline precipitates were obtained, which, dried at 212°, possessed a composition corresponding to the formulæ $2BaO, HO, AsO^5 + 2HO$ and $2SrO, HO, AsO^5 + 3HO$.

By the addition of arsenic acid to acetate of magnesia, or by precipitating sulphate of magnesia with arseniate of soda, a salt of mag-

nesia was obtained having the formula $2MgO, HO, AsO^5 + 13HO$ which on washing with much water parted with some acid, and furnished the basic salt $3MgO, AsO^5$.—*Journ. für Prakt. Chem.*, xlix. p. 182.

ANALYTICAL CHEMISTRY.

On the Estimation of Ammonia. *By* Th. Schlœsing.

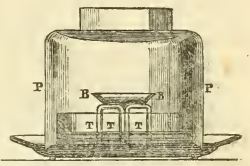
Previous to the recent researches of Boussingault on the proportion of ammonia contained in urine, chemists were not possessed, as far as I am aware, of a very accurate process for estimating this base when accompanied with nitrogenous substances. However good a method of analysis may be, any other method of accomplishing the same object deserves being made known; and this leads me to hope some interest may attach to the following, which I have applied to the examination of tobacco, and have shown that the presence of nitrogenized substances does not interfere with its accuracy.

It is known, that, notwithstanding the great affinity of water for ammonia, when saturated with this gas, it is entirely deprived of it by mere exposure to the air. This fact is so well known, that I abstain from further detail, and will merely relate one experiment proving that the most dilute ammoniacal solutions disengage ammonia, which may be used to ascertain the presence of minute quantities of it in a liquid. Some water rendered alkaline by lime, and containing a very minute quantity of ammoniacal salt, is poured into a bottle; and above the liquid is suspended, by being wedged in between the stopper, a piece of moist reddened litmus-paper. If the water contain $\frac{1}{30000}$dth part in weight of ammonia, the paper turns blue in a few moments, and in a few minutes when it contains $\frac{1}{100000}$dth; the blue colour still appears, but only after about a quarter of an hour, when it contains $\frac{1}{250000}$dth.

Since the ammoniacal gas is entirely disengaged from an aqueous solution by exposure to the air, it is certain that it will be liberated, although more slowly, when placed under a bell-glass over sulphuric acid; after a certain interval the acid will have absorbed the whole of the ammonia; and if its strength be known, it will suffice, in order to ascertain the amount of the base, to neutralize the excess of acid with a solution of known strength of saccharate of lime. When the ammonia is combined with an acid, it will only be necessary to expel it by a fixed base, lime or potash.

The only objection which can be made to this process, which is otherwise extremely simple, and merely demands a few minutes' care on the part of the operator, is the time it requires. It will be conceived that the duration of the total absorption of ammonia by the sulphuric acid must depend on several circumstances, and especially on the amount of ammonia to be absorbed, on the concentration and extent of surface of the solution, of the extent of surface of the sulphuric acid, of the temperature, capacity of the bell-glass, of the arrangement of the vessels in its interior, which must be more or less favourable to the circulation of the ammoniacal vapours.

The ammoniacal solution is contained in a vessel, A, which should be flat with slightly elevated borders, and from 10 to 12 centims. diameter; shallow glass evaporating dishes answer exceedingly well. The vessel A is placed over mercury contained in the hollow of a plate upon a glass tripod T, 3 centims. in height. Situated in the centre of the vessel A is the vessel B, containing sulphuric acid; any shallow saucer having a diameter of from 6 to 7 centims. will do perfectly well. Instead of a bell-glass I use a strong glass shade, P; a weight placed on it sinks it in the mercury, and compels it to rest on the plate.



The following is an example of the kind of experiments first made with the assistance of this apparatus. In the vessel A a known weight of an ammoniacal salt was placed, which was then dissolved in water. Having arranged the vessel containing the acid upon its tripod, the shade over the whole was raised on one side, so as to be able to introduce between its margin and that of the vessel A the extremity of a pipette full of milk of lime. The jet of the pipette sufficed to mix this alkali with the dissolved ammoniacal salt. As soon as the lime was poured in, the margin of the bell-glass was immersed in mercury, and the weight placed on the top of it. After a variable amount of time, the experiment was discontinued, and the quantity of ammonia absorbed, determined by means of saccharate of lime.

We have not thought it worth while to enumerate the author's experiments, but have confined ourselves to the conclusions which he has drawn from them:—

1. The quantity of ammonia absorbed in a certain time is the more considerable the more concentrated the solution; the rapidity of the absorption will therefore be assisted by reducing as much as possible the bulk of the ammoniacal solution.

2. In proportion as the absorption advances, the quantities of ammonia absorbed within equal times go on decreasing; in fact, the tension of the ammoniacal gas becomes more and more weak.

3. When the volume of the ammoniacal solution does not exceed about 35 cub. centims., and contains little or much ammonia, it contains but a few milligrammes after twenty-four hours.

4. A few milligrammes of ammonia, dissolved in from 25 to 35 cub. centims. of water, are only entirely absorbed by the acid at the end of about twenty-four hours.

On the whole, when a quantity of ammonia amounting to between 100 milligrms. and 1 grm. is dissolved in from 25 to 35 cub. centims. of water, and introduced into the above-described absorption apparatus, the greater portion of the ammonia is absorbed in the few first hours; after twenty-four hours the whole is absorbed excepting a few milligrammes, the complete absorption of which requires twenty-four hours further. Thus a determination of the

amount of ammonia will require about forty-eight hours, and will depend rather on the bulk of the ammoniacal solution than on the quantity of the base itself.

The process was verified by applying it to known quantities of different pure and well-defined salts of ammonia. These experiments were made in the following manner:—The amount of water in which the ammoniacal salt was dissolved was always comprised between 25 and 35 cub. centims. The ammonia was expelled sometimes by lime, sometimes by potash. When lime was employed, it was always poured into the ammoniacal salt, only the pipette was not drawn out to a point, in order that the addition of the lime being almost instantaneous, the ammonia should not have time to escape. When potash was used, no loss of ammonia was possible, as a piece of potash was placed upon a small glass tripod arranged in the centre of the ammoniacal solution; it soon became liquefied in the moist atmosphere, but not before every issue was closed. Before discontinuing each experiment, a piece of moist reddened litmus-paper was introduced under the bell-glass, to be certain that the absorption of the ammonia by the acid was complete. Lastly, when, in the neutralization of the acid by the saccharate of lime, the point of neutrality was exceeded, the liquid was restored to a suitable degree of coloration by means of a solution of sulphuric acid ten times more dilute than the acid which had been used for the absorption.

Experiments:—

I. 0·621 grm. sulphate of ammonia, containing theoretically 160 milligrms. of ammonia; the ammonia was expelled by lime; the experiment lasted forty-eight hours:—

	Cub. centims.
Sulphuric acid. (Strength, 25 grms. of real acid in 1 litre.)	17·09
Saccharate of lime (Strength, 68 cub. centims. to 100 of acid.)	1·42
Sulphuric acid, 10 times more dilute (Strength, 2·5 grms. of acid in 1 litre.)	0·78

Whence ammonia found 160·3 milligrms.

II. 0·868 grm. of the same sulphate, containing theoretically 223·58 milligrms. ammonia; the ammonia was expelled by lime. Experiment lasted forty-eight hours. Ammonia found, 223·46.

III. 0·541 neutral oxalate of ammonia furnished 129·23 milligrms. of ammonia. Theory requires 129·5.

IV. Bimalate of ammonia, obtained from tobacco, $C^8\,H^4\,O^8\,NH^3$, HO, dried for twenty-four hours over sulphuric acid. In the first experiment, the ammonia having been expelled by lime, the solution formed after some time a transparent jelly; this semisolid state retarded the liberation of the ammoniacal gas, for after forty-eight hours only 149 milligrms. out of 153 were found. In a second experiment, the ammonia was expelled by potash, the solution remained liquid, and the ammonia was completely absorbed in forty-eight hours. 1·061 grm. of the salt, containing theoretically 119·5 milligrms. of ammonia, gave 119·6.

Instead of measuring the sulphuric acid with a burette, a known weight of an acid, the strength of which has previously been determined by analysis, may be employed for the absorption of the ammonia. The author enumerates a number of experiments, which satisfactorily prove the accuracy of the method employed when applied to pure and soluble salts of ammonia.

With respect to the insoluble salts of ammonia, the author has hitherto examined only that which is of most frequent occurrence, the subphosphate of ammonia and magnesia; it is dissolved in nitric acid, which is preferable to hydrochloric acid, usually employed for dissolving the phosphates, as the chloride of calcium retards the liberation of the ammonia. Moreover, when any considerable amount of phosphate is present, the solution must be mixed with some inert substance, for instance powdered tobacco exhausted with water; otherwise, where the alkali falls, a thick magma is often formed, which encloses a portion of the phosphate and protects it from the action of the lime, which is not the case when it is mixed with some inert substance. Notwithstanding these precautions, the disengagement of the ammonia is exceedingly slow; thus it required seventy-two hours for the complete absorption of the ammonia contained in 1·5 grm. of the phosphate. However, when the ammoniophosphate of magnesia occurs in an organic substance, it is almost always in small quantity, and in such a state of division that it is completely decomposed by lime, without its being necessary to dissolve it in an acid.

The author then made some experiments to ascertain whether the presence of certain substances capable of combining with ammonia might not retard the disengagement of that base after its elimination by a fixed alkali, and even entirely prevent it.

Chloride of Calcium.—An ammoniacal salt, containing 210 milligrms. of ammonia, was mixed with 2 grms. of chloride of calcium dissolved in 35 cub. centims. of water; the ammonia was expelled by milk of lime. After forty-eight hours the sulphuric acid had absorbed only 206·4 milligrms. of ammonia. Reddened litmus-paper, introduced under the bell-glass at the conclusion of the experiment, was quickly turned blue. Thus the chloride of calcium retards the disengagement of the ammonia, without however preventing it. When its presence is known, it will be advisable to decompose it by a sufficient quantity of oxalate of potash, and to expel the ammonia by potash.

Sulphates of Copper and Nickel.—In these experiments the loss amounted respectively to 1·7 milligrm. and 1·2, but the volume of each solution amounted to 45 cub. centims.; so that the losses may be ascribed rather to the great bulk of the solutions than to any retardation caused by the presence of the oxides of copper and nickel.

Nitrate of Silver and Corrosive Sublimate.—Oxide of silver forms with ammonia a compound which retains this base; and when an alkali is added to a mixture of corrosive sublimate and an ammoniacal salt, white precipitate is formed, which equally retains some ammonia. The formation of these two compounds is avoided by

mixing with the potash used to liberate the ammonia a sufficient quantity of sulphuret of potassium to precipitate the whole of the silver or mercury.—*Ann. de Chim.*, Feb. 1851.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Action of Chloride of Ammonium in the Oxidation of Colouring Matters by Salts of Copper. By Messrs. C. Kœchlin *and* E. M. Plessy.

The muriate of ammonia facilitates in a remarkable manner the oxidation of colouring substances by the oxysalts of copper, and we therefore generally find it associated with these salts in the majority of the topical colours. The experiments we are about to describe will explain the theory of this reaction.

When a strip of copper is immersed in a solution of acetate of copper out of contact with the air, there is, as is well known, no reaction; but add muriate of ammonia (twice the amount in weight of the copper salt) to this solution, and notwithstanding the air is excluded, the liquid becomes spontaneously colourless*; by cooling, small white crystals are precipitated, which exhibit all the characters of the protochloride of copper. If we now remove the strip of metal, and agitate the solution in the presence of air, it will reacquire its primitive colour, and binoxide of copper be again formed.

A little reflection, and we shall readily perceive what is the function of the chloride of ammonium when it is employed concurrently with the copper salt in the presence of an organic colourable principle. This principle evidently holds the place of the metal in the experiment above related; oxide of copper is reduced. But upon the stuffs, the reaction, under favourable circumstances in a moist atmosphere, does not stop there; after the first reduction, there remains a compound, which, owing to its property of dissolving oxygen, is well adapted to furnish a further inducement to the oxidation of the colouring principle. The advantage resulting from the employment of the chloride of ammonium, when it is requisite to use but a small quantity of oxide of copper with a substance which would require a rather large amount of oxidizing agent in order to avoid an unfavourable colouring of the lake deposited on the tissue, is at once evident. This is what is done at St. Marthe for the rose tints; only a small quantity of the copper salt is introduced into these rose colours, which the presence of the hydrochlorate of ammonia renders sufficient with a suitable exposure to a moist atmosphere.

In this case are we not justified in admitting that the oxide of copper acts as the means of continually transferring the oxygen of the atmosphere to the colouring principle? What appears to confirm this hypothesis is, that a red, left for several weeks without washing after it has attained its maximum of colour, degenerates even to

* M. Levol's method of estimating copper is founded upon this reaction.

a pale brown, passing successively through more and more oxidized tints*.

Nothwithstanding the advantage presented by the ammonia salt of enabling us to oxidize with small quantities of the copper salt, the employment of this salt is not free from inconveniences, in the case of certain steam colours, where it may give rise to too powerful an oxidation however minute the quantity employed.

According to what precedes, if the protocompound of copper produced by the reaction of the persalt in the presence of chloride of ammonium and a strip of copper is able to absorb oxygen from the air, this compound may, like the binoxide, be adapted to the oxidation of a colouring substance. This is, in fact, what we observe.

250 grms. of sulphate of copper and 375 grms. of chloride of ammonium were dissolved in sufficient water to form a quart. A portion of this solution was reduced by slips of copper, the other was preserved as it was. On the other hand, a catechu colour was prepared of 200 grms. to the quart, and suitably thickened. A decilitre of each solution of copper was poured into equal volumes of the colour, a pint in each. Some stuffs were printed at once, and steamed after sufficient exposure to the air. After the steaming, we observed the effect we had expected; the oxidation was most advanced in the case of the liquor which had been reduced. This will not appear surprising when we consider, according to what has been stated above, that the dissolved oxide of copper having to furnish oxygen from itself and from the air, whence it takes it, the oxidation of the colouring matter must proceed more rapidly where there is most metal, the oxygen remaining the same in the copper salt; and that is what takes place in our solution of copper when a metal has been inserted in it. Some copper is dissolved, but nothing else is changed in the absence of the air; but admit that, and a quantity of binoxide of copper will be formed double that which was in solution, and capable of furnishing twice the amount of oxygen, according to the formula $CuO^2 + Cu = Cu^2O^2$, which in the presence of $+O^2$ becomes Cu^2O^4.

We now perceive the chief peculiarity of the mixture of a salt of copper with chloride of ammonium; as regards the question under consideration, it is to facilitate the oxidation of a colouring principle. But if it is proved that the hydrochlorate of ammonia increases the oxidizing power of a salt of copper, it is not known whether any other salt of ammonia will produce an analogous effect. The following experiments were made for determining this point.

To equal quantities of caustic ammonia, saturated by different acids, the same bulk of a normal solution of catechu is added containing a quantity of sulphate of copper equal to one-fourth of the weight of the colouring matter. For the sake of clearness, we shall designate by numbers the acids with which we experimented; these numbers hereafter will indicate the colours submitted to impression:—

* Certain ferruginous colours, steam or topical, exhibit a spontaneous combustion of this kind. Thus we frequently find the most intense logwood blacks pass in the course of time into pale brown, although they have been kept protected from atmospheric influences.

1. Hydrochloric acid
2. Nitric acid
3. Acetic acid
4. Sulphuric acid
5. Oxalic acid
6. Tartaric acid
7. Citric acid

} in a given volume of caustic ammonia.

These different salts of ammonia were mixed with the normal solution of catechu. A volume of this normal solution was put by, in order to see what the copper salt alone would effect in the oxidation of the colouring matter. Moreover, as in the present case the experiments are comparative, they were made so as to have with equal volumes always the same quantity of colouring matter. As to the copper salt, its amount is always the same, since it forms part of the normal solution of catechu, of which a constant volume is taken.

The colour which contains no salt of ammonia, but only the copper salt, was marked with the sign 0.

After the impression, the stuffs are exposed to the air for some days, when it is seen that the colours 0, 4, 5, 6, 7 are of the same depth; the numbers 2 and 3 are deeper than the preceding; and lastly, number 1 exhibits, in comparison with numbers 2 and 3, a considerable development in the depth of the colour. We think we may therefore conclude, that in number 1 there was oxidation; in numbers 2 and 3 the escape of a volatile acid, rather than oxidation, seems to us to have raised the depth of the colour; and in the remainder, 0, 4, 5, there was no change.

These colours were then steamed, and the same differences were perceptible; number 1, that is to say the colour containing chloride of ammonium, was much the deepest. Thus the hydrochlorate of ammonia is, of all the salts of ammonia, the only one which acts powerfully in the oxidation of a colouring matter. On the other hand, we have already observed, that in the presence of metallic copper and a salt of copper, it readily determines a reduction of the salt. Connecting these two facts, we have been led to examine comparatively the influence of the chloride of ammonium, and that of our ammoniacal solutions 2, 3, 4, 5, on the reduction of a copper salt by metallic copper; and we found that of all these solutions none exhibited the reaction observed with the chloride of ammonium. This valuable property of this salt justifies the parallel we drew between a reducing metal and a colouring principle; for it may be here remarked, that we have two series, one with a metal, the other with a colourable principle, and that, everything else being alike, the results agree, and prove that the action of the ammoniacal salt is quite peculiar, and that this action is exerted in the same manner in the presence of a reducing substance whether it be metal or colourable principle. Having ascertained the nature of the action of the ammonia salt upon a salt of copper, and it being shown that the ammonia takes no part in the action, we may ask whether any other chloride, culinary salt for instance, would not produce an analogous effect. This question was answered in the affirmative by

the following experiment:—Some chloride of sodium was added to the normal solution of catechu above mentioned, and to another portion some muriate of ammonia. Excepting the lustre of the tint, and that is the sole difference, the results appeared similar as regards the oxidation, which was as decidedly advanced in the one case as in the other.

The preceding experiment clearly demonstrates the effect of the chloride of ammonium in the case of a colour where a salt of copper is present; it undoubtedly acts like any other chloride, producing double decomposition, whence results the bichloride of copper. When once the salt is formed, the muriate of ammonia takes no further part in the oxidation of the colouring matter. We therefore imagined that the property which the protochloride of copper possesses of dissolving in water charged with chloride of ammonium, might establish between that salt and the chloride of sodium a perceptible difference; but our experiments on the subject show nothing of the kind. The chloride of sodium acts like the chloride of ammonium. The action of this last salt is the production of the bichloride of copper, which is better suited than any other salt of copper for the oxidation of a colouring matter. This is proved by the following experiment:—Introduce into two equal quantities of a thickened solution of catechu, into the one bichloride of copper and into the other sulphate, and it will be seen, by simple exposure to the air, or better still after the steaming, that in the case of the chloride of copper the colour is highly developed, and that there only oxidation has taken place.

In conclusion, the muriate of ammonia in those colours, where it is employed, is, in our opinion, destined to produce double decomposition, from which results bichloride of copper, the oxidizing action of which upon these colouring matters is remarkably powerful.

Any other chloride, chloride of sodium, potassium, calcium, tin, &c., may be substituted for the chloride of ammonium.—*Journ. de Pharm.*, Dec. 1850.

Observations on Nitrous Acid and a Nitro-sulphuric Acid Solution. *By* M. Guinon.

In endeavouring to ascertain the cause of an accident which had happened to a bath of rose-colour for dyeing silk made with an ammoniacal solution of cochineal, and which had suddenly become decolorized, I found that this decoloration was due to the presence of some nitrous acid in the sulphuric acid employed. I was certain, that, if the sulphuric acid had been pure, it would not have altered the ammoniacal solution of cochineal, even by several days' contact, as I had frequently found from experience. Nitric acid alone would merely have turned the colour into an orange-red, without destroying it. I could therefore only attribute the action observed to the presence of hyponitric acid, which is sometimes met with in the commercial sulphuric acid; and I proceeded to verify it synthetically. I passed nitrous vapours into pure sulphurous acid, and obtained in this manner a reagent (nitrosulphuric acid) which immediately decolorized the cochineal dye. In this reaction it is

evident that the nitrosulphuric mixture acts by means of the nitrous acid which is formed. The instability of this acid and its tendency to part with oxygen, render it eminently suited to alter and oxidize organic matters.

Besides what I had observed upon cochineal, I wished to extend my experiments to the action of the nitrosulphuric acid upon several salts and various colouring substances. The following are the results:—

Dilute solutions of the colouring substances and of salts.	Nitrosulphuric solution.
Ammoniacal cochineal	Decoloration.
Safflower	Decoloration.
Red woods with chloride of tin	Decoloration.
Logwood with chloride of tin	Decoloration.
Indigo.....	Decoloration.
Turmeric	Decoloration.
Annotto	Decoloration.
Protosulphate of iron.....	Formation of persulphate, absorption of deutoxide of nitrogen, which strikes a brown colour.
Protochloride of tin	Formation of perchloride.
Yellow prussiate of potash..	Production of red prussiate, disengagement of deutoxide of nitrogen.
Cyanide of iron	Great increase of colour.
Bichromate of potash	Greenish colour, formation of sulphate of potash and nitrate of chrome.

I found in these experiments that the solution of the nitrous acid in the sulphuric acid might be highly diluted with water without losing its properties. Indeed a sufficient quantity of water is even requisite, in order to avoid the production of the deutoxide of nitrogen and to keep the liquid at a low temperature on mixing the two acids.

The nitrosulphuric acid mixture has the property of decolorizing in the highest degree by means of the nitrous acid to which it gives rise, and which it contains as it were in the latent state. It presents in the smallest volume one of the most powerful decolorizing agents. I have found that a cold and highly-diluted solution bleaches silk almost instantaneously, which will permit of its being employed for this purpose the more advantageously, as nitrous acid is reproduced successively by contact with the air.

This solution may be very cheaply obtained, by collecting in concentrated sulphuric acid the nitrous vapours which are disengaged in acting upon various metals (copper, tin, mercury, &c.) by nitric acid, or still more simply by the action of nitric upon oxalic acid.

An ammoniacal solution of cochineal will detect the presence of less than one two-thousandth part of nitrous acid in a solution. It is a more special and more certain reagent than the protosulphate of iron, which merely shows the presence of nitrous products in general.—*Comptes Rendus*, Feb. 17, 1851.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Stibmethyle. *By* H. LANDOLT.

THE author has prepared and examined, at the suggestion of Prof. Löwig, the compound of methyle analogous to stibæthyle. The same apparatus was used for its preparation as that described by Löwig and Schweitzer in their investigation on stibæthyle*. Pure anhydrous iodide of methyle, obtained by the concurrent action of iodine and phosphorus upon wood-spirit, was submitted to distillation with a mixture of quartz-sand and the alloy of antimony and potassium in a small flask. In general a violent reaction immediately took place, in the course of which the excess of iodide of methyle was volatilized, after which the stibmethyle was distilled over by the gradual application of heat.

In its physical characters stibmethyle agrees perfectly with stibæthyle. It forms a heavy colourless liquid, of a peculiar odour, which is insoluble in water, sparingly soluble in alcohol, but readily in æther. Exposed to the air, it gives off dense white fumes, takes fire, and burns with a white flame, with elimination of metallic antimony.

The series of compounds of stibmethyle likewise corresponds to those of stibæthyle. It combines with 2 atoms of oxygen to form a base, which saturates 2 atoms of acid, and it also gives the corresponding compounds with S^2, Cl^2, Br^2, I^2, &c. The properties of these compounds do not differ essentially from those of the corresponding compounds of stibæthyle.

When, in the preparation of stibmethyle, the iodide of methyle which first passes over, and the stibmethyle which escapes at a higher temperature, are collected in the same vessel, a slight ebullition is perceptible, and in a short time the liquid mixture becomes converted into a perfectly white crystalline mass.

In their paper on stibæthyle, Löwig and Schweitzer state that crystals frequently form in the first portions that pass over, which they considered to be the iodide of stibæthyle; but they obtained too small a quantity to submit it to analysis. An examination of the crystals obtained with stibmethyle showed that they do not belong to the stibmethyle series, but correspond to the formula $StMe^4 + I$. They are very easily obtained when pure iodide of methyle

* Chem. Gaz., vol. viii. pp. 201, 372.

is added in drops to stibmethyle. No other products are formed. In this respect, therefore, stibmethyle and also stibæthyle are related to ammonia; for it is beyond all doubt that the crystals mentioned by Löwig and Schweitzer in their paper also correspond to the formula $StAe^4+I$; and indeed iodide of æthyle added to stibæthyle produces the same crystals. Further, æthyle and methyle mutually replace each other in these compounds; thus, for instance, crystals were obtained by adding iodide of methyle to stibæthyle, which corresponded to the formula $StAe^3Me+I$. The researches on this series have yielded as the most important result, that a compound consisting of $(StMe^4)O$ can be isolated; thus furnishing a complete confirmation of the ammonium theory. The compound $StMe^4$ the author has named stibmethylium.

Oxide of Stibmethylium, $(StMe^4)O$.—To obtain this base, recently-precipitated oxide of silver is added to the aqueous solution of the corresponding iodide, $(StMe^4)I$, until no more iodide of silver is formed. On evaporating the solution over sulphuric acid under the air-pump, a white crystalline mass remains, which as regards alkalinity agrees completely with hydrate of potash. It has the same soapy touch between the fingers as the hydrate of potash, is exceedingly caustic, very readily soluble in water and alcohol, but insoluble in æther. When the solution is evaporated in the air, it absorbs carbonic acid, and then strongly effervesces with acids, and on the addition of lime-water gives a precipitate of carbonate of lime. When a glass rod moistened with muriatic acid is held over the solution, white fumes are perceptible; nevertheless the base is not very volatile, for almost the entire amount remains even on evaporating the solution on the water-bath. When the compound is quickly heated in a glass tube closed at one end, vapours are given off, which ignite in the air with separation of metallic antimony; but on carefully heating, the dry base is volatilized without decomposition. The aqueous solution has a ley-like odour and taste, and instantly turns red litmus-paper blue. Ammonia is instantly expelled in the cold, and baryta is incapable of separating the base from its combination with iodine. Lime and oxide of lead are instantly precipitated by the oxide of stibmethylium; a white precipitate is produced in a solution of a salt of the oxide of zinc, which redissolves in an excess of the precipitant; salts of copper furnish a precipitate of the hydrated oxide, which does not dissolve in an excess; protosalts of mercury give a black, the persalts a yellow precipitate; in salts of silver a brownish-black precipitate is formed, insoluble in an excess of the precipitant; in chloride of platinum, a yellow precipitate, as with potash. When a concentrated aqueous solution of the oxide of stibmethylium is boiled with sulphur, a yellow liquid is obtained; and on mixing this with a dilute acid, milk of sulphur separates, with disengagement of sulphuretted hydrogen. Altogether this substance agrees so closely with potash, that it would certainly be taken for it in a merely qualitative examination.

The oxide of stibmethylium forms with acids neutral and acid salts, which as far as the observations go agree entirely with the salts of

potash, and are indeed isomorphous with them. Some of them are obtained directly, others by double decomposition.

Bisulphate of the Oxide of Stibmethylium, $(StMe^4)O,HO+2SO^3$. —When to a solution of the iodide, $(StMe^4)I$, a boiling solution of sulphate of silver is added, so long as a precipitate of iodide of silver results and the filtered solution is evaporated on the water-bath, the salt is obtained in beautiful quadratic prisms with truncated edges. The crystals are very hard, readily soluble in water, and likewise pretty readily so in alcohol. They have an acrid acid taste, with a bitter after-taste.

When the concentrated solution of the acid salt is saturated with oxide of stibmethylium, the acid reaction entirely disappears; and on mixing now the aqueous solution with a mixture of æther and alcohol, the neutral salt separates in oily drops, which after some time solidify in the air; it forms four-sided prisms, and is consequently isomorphous with the sulphate of potash.

Nitrate of the Oxide of Stibmethylium.—This compound is prepared in the same manner as the sulphate, with the use of nitrate of silver. It is readily soluble in water, astringent, and at the same time has a bitter taste; it crystallizes in minute needles, and detonates on the application of heat.

Bicarbonate of the Oxide of Stibmethylium is obtained when the aqueous solution of the base is completely saturated with carbonic acid gas; it crystallizes in stellate groups of slender needles, is easily soluble in water, has a slight alkaline bitter taste, and gives no precipitate with neutral salts of magnesia.

Iodide of Stibmethylium, $(StMe^4)I$.—This is always formed when iodide of methyle is mixed with stibmethyle. The white crystalline mass obtained is dried between paper, and then recrystallized from water or alcohol, in which it is readily soluble; it separates in very beautiful six-sided prisms. It is sparingly soluble in æther; it has a saline bitter taste. When heated in a tube closed at one end, it gives off vapours which are spontaneously inflammable in the air, and at the same time deposit antimonious acid. The iodine can be separated by a salt of silver from an aqueous solution. With a solution of corrosive sublimate, it furnishes a precipitate of iodide of mercury, with production of chloride of stibmethylium. Acids eliminate iodine.

Chloride of Stibmethylium, $(StMe^4)Cl$, is obtained by evaporating the iodide with concentrated muriatic acid, or by decomposing it with a solution of corrosive sublimate, but best of all by saturating a solution of the pure oxide with muriatic acid. White crystals are left on evaporation, which are readily soluble in water, less so in alcohol, and not at all in æther. They have a bitter taste, and in other respects resemble the iodide.—*Mittheil. der Naturforsch. Gesellsch. zu Zurich*, 1851, No. lxiv.

On a new Method of preparing Carbonic Æther. *By* A. Wurtz.

M. Ettling obtained carbonic æther by acting with potassium upon oxalic æther. Hitherto, as far as I am aware, no other method

has been described for preparing this substance, which it is impossible to procure by the processes generally adopted for the preparation of the compound æthers. In studying, some years ago, the action of chloride of cyanogen upon alcohol, I noticed the formation of urethane in this reaction, which at the same time furnishes a considerable quantity of chloride of ammonium. The production of ammonia under these circumstances indicates the complete decomposition of the elements of the chloride of cyanogen, C^2 NCl, by the molecule of water of the alcohol C^4 H^5 O, HO, or rather by the water which is added to the mixture to facilitate the reaction. At the same time that the hydrogen of this water unites with the nitrogen and the chlorine of the chloride of cyanogen, its oxygen combining with the carbon should give rise to the formation of 2 equivs. of carbonic acid: it will easily be conceived that this carbonic acid being in the nascent state in the presence of oxide of æthyle formed by the dehydration of the alcohol, will combine and form carbonic æther. This, in fact, is what happens. In order to isolate the æther, the liquid obtained by the reaction of the chloride of cyanogen upon weak alcohol is mixed with water, and an oily layer separates on the surface, which contains carbonic æther. On submitting this ætherial liquid to distillation, its boiling-point rises gradually from 176° to 257° F. If what comes over above 248° is collected separately, it will be found to be carbonic æther, with which it agrees in its odour, its boiling-point (259°), and in composition, which is placed beyond doubt by the following analysis:—

Carbon	50·70	50·68	10 =	60	50·81
Hydrogen	8·31	8·66	10	10	8·47
Oxygen	..	..	6	48	40·72

The reaction of chloride of cyanogen upon alcohol is consequently expressed by the following formulæ—

$$C^2\,NCl + C^4\,H^6\,O^2 + 2HO = \underset{\text{Urethane.}}{C^6\,H^7\,NO^4} + HCl.$$

$$C^2\,NCl + 2C^4\,H^6\,O^2 + 2HO = \underset{\text{Carbonic æther.}}{C^{10}\,H^{10}\,O^6} + H^4\,NCl.$$

The hydrochloric acid may act upon another portion of the alcohol, and give rise to the production of a certain quantity of hydrochloric æther.—*Comptes Rendus*, April 21, 1851.

On a new Class of Æthers. *By* G. Chancel.

In a previous communication* I described a process by means of which I had succeeded in producing several ætherial compounds hitherto without representatives in chemistry. The process is founded on the double decomposition of the sulphovinates, and other vinic salts, under the influence of heat. As these vinates are produced by polybasic acids, such as sulphuric, carbonic, oxalic and

* Chem. Gaz., vol. viii. p. 454.

succinic acids, I hoped to obtain true double æthers with the latter acids; and I have succeeded in preparing double oxalates, carbonates and sulphocarbonates of æthyle and methyle, of æthyle and amyle, and of methyle and amyle. I shall now describe their principal characters and the method of preparing them:—

Oxalate of Æthyle and Methyle is obtained by distilling at a gentle heat an intimate mixture of equal parts of anhydrous oxalovinate and sulphomethylate of potash. It is a colourless liquid, which partakes of the properties of the oxalates of æthyle and methyle as regards density, boiling-point, &c. Boiling water dissolves it entirely, decomposing it into oxalic acid, alcohol and wood-spirit. With ammonia it furnishes a precipitate of oxamide. Its analysis led to the formula $C^5 H^8 O^4 = C^2 O^4 EtMe = 2$ vols.

Oxalate of Æthyle and Amyle is prepared in a similar manner by the decomposition of the oxalovinate and sulphamylate of potash.

Oxalate of Æthyle and Amyle is procured by distilling a mixture of oxalamylate and sulphomethylate of potash.

Carbonate of Æthyle and Methyle is obtained by submitting to a gentle heat a mixture of carbovinate and sulphomethylate of potash. It is a colourless limpid liquid, possessing nearly all the properties of the ordinary carbonic æther, from which however it differs by a higher specific gravity and a lower boiling-point.

The same process may be employed for the production of carbonic æther itself, which has hitherto been obtained only by the action of potassium upon oxalic æther. I prepare carbonic æther by heating a mixture of carbovinate and sulphovinate of potash; my method is consequently applicable to the direct ætherification of carbonic acid.

Sulphocarbonate of Æthyle and Methyle is very easily obtained by distilling an intimate mixture of anhydrous xanthate and sulphomethylate of potash. It is a limpid liquid, of a pale yellow colour, sweetish taste, and of a strong ætherial odour, which is not disagreeable. It contains $C^4 H^8 OS^2 = COS^2 EtMe = 2$ vols.

It is known, from the interesting observations of M. Cahours, that carbonic æther is converted into urethane and alcohol under the influence of ammonia. The sulphocarbonate of æthyle and methyle undergoes a similar metamorphosis, and furnishes, instead of urethane, sulphuretted urethane; and instead of alcohol, methylic mercaptan.

The *sulphuretted urethane* thus obtained forms beautiful colourless prisms, fusible at 96° F., soluble in water, and especially so in alcohol and æther. Its composition is represented by that of mercaptan, in which the half of the oxygen is replaced by sulphur. It consequently possesses the composition and properties of xanthamide described by M. Debus*, and which that chemist obtained by a totally different process. This remarkable action of ammonia on the sulphocarbonate of æthyle and methyle exhibits the parallelism existing between the carbonic and sulphocarbonic æthers, as well as between the alcohols and mercaptans.—*Comptes Rendus*, April 21, 1851.

* Chem. Gaz., vol. viii. p. 146.

*Supplementary Observations on the Diffusion of Liquids**.

By Thomas Graham, F.R.S., F.C.S.

The former experiments of the author furnished strong grounds for believing that isomorphous salts possess a similar diffusibility. All the salts of potash and ammonia, which were compared, appear to be equi-diffusive; so also were the salts of certain magnesian bases. A single preliminary observation on the nitrates of lead and baryta, however, opposed the general conclusion, and demanded further inquiry. It is scarcely necessary to say that any new means of recognizing the existence of the isomorphous relation between different substances, must prove highly valuable. The investigation was also extended to several new substances, such as hydrocyanic acid, acetic acid, sulphurous acid, alcohol, ammonia and salts of organic bases, without reference to isomorphous relations.

Hydrogen Acids.—The period of diffusion arbitrarily chosen for these acids was five days. The diffusate, or quantity of acid diffused, was determined by precipitating the liquid of the external reservoirs with nitrate of silver, and weighing the salt of silver formed.

Diffusion of hydrochloric acid in five days, at 51° F., in two cells:—

	Grs.	Ratio.
From 1 per cent. solution	7·41	0·97
From 2 per cent. solution	15·04	2·00
From 4 per cent. solution	30·72	4·08
From 8 per cent. solution	67·68	9·00

Hydrochloric acid is the most highly diffusive substance hitherto observed; it appears to exceed hydrate of potash at 53°·5, as 7·56 to 6·12, or as 100 to 80·9.

The experiments indicate a similarity of diffusion between the isomorphous substances, hydrochloric and hydriodic acids, and hydrochloric and hydrobromic acids.

Diffusate from 2 per cent. solutions at 51° F.:—

Hydrochloric acid	15·04	100
Hydriodic acid.....	15·11	100·46

Diffusate from 2 per cent. solutions at 59°·7 F.:—

Hydrochloric acid	16·55	100
Hydrobromic acid	16·58	100·18

Hydrobromic acid appears therefore to coincide in diffusibility with hydrochloric acid at this temperature. It is remarked that these three acids, hydrochloric, hydrobromic and hydriodic, do not exhibit the same correspondence in another physical property, namely, the densities of their aqueous solutions containing the same proportion of acid. The densities of 2 per cent. solutions of hydrochloric and hydriodic acids appear to be respectively 1·0104 and 1·0143, at 60° F., and that of hydrobromic acid is an intermediate number. The same acids are also known to differ considerably in the boiling-points of solutions containing the same proportion of

* An abstract of the author's former paper was given in vol. viii. p. 38.

acid. A considerable diversity of physical properties appears here to be compatible with equal diffusibility in substances which are isomorphous.

The diffusion-time of bromine was made ten days, or double the time of hydrobromic acid. Two cells contained together a diffusate of 5·80 grs. of bromine; another two cells a diffusate of 5·88 grs.; mean 5·84 grs. at 60°·1 F.; or 6·76 grs. for a 1 per cent. solution. Doubling the last result, 13·52 grs. are obtained for a 2 per cent. solution, which is still considerably under the diffusate of hydrobromic acid (16·58 grs.) in half the time.

Hydrocyanic acid appeared less diffusive than hydrochloric acid, at the same temperature 59°·7, as 12·45 to 16·55, or as 75·2 to 100, and not to belong therefore to the same class of diffusive substances.

Nitric Acid.—Time of diffusion also five days. The quantity of this acid diffused was determined with great exactness by neutralization by means of a normal solution of carbonate of soda.

The diffusion of the different proportions of this acid at one temperature is as follows.

Diffusion of nitrate of water in five days at 51°·2; two cells:—

	Grs.	Ratio.
From 1 per cent. solution	6·99	0·95
From 2 per cent. solution	14·74	2
From 4 per cent. solution	28·76	3·90
From 8 per cent. solution	57·92	7·86

The 2 per cent. solution is taken as the standard of comparison for the ratios, instead of the 1 per cent. solution, from the greater accuracy with which the diffusion of the former can be observed.

The usual approach to equality of diffusion, between chlorides and nitrates, is observable in hydrochloric and nitric acids, at least in the 1 and 2 per cent. solutions.

Sulphuric Acid.—The time of diffusion arbitrarily chosen for this and the three following acids was ten days. The diffusate of this acid was determined in the same manner as that of nitric acid.

The diffusion of the different proportions of sulphuric acid is as follows.

Diffusion of sulphate of water in ten days at 49°·7; two cells:—

	Grs.	Ratio.
From 1 per cent. solution	8·69	1·03
From 2 per cent. solution	16·91	2
From 4 per cent. solution	33·89	4·01
From 8 per cent. solution	68·96	8·16

The diffusibility of different strengths of this acid appears to be pretty uniform, but with a slight tendency to increase in the higher proportions, like hydrochloric acid.

Sulphuric acid is greatly inferior in velocity of diffusion to hydrochloric acid, but still appears to possess considerably more than half the diffusibility of the latter.

Chromic Acid.—The diffusate of the 2 per cent. solution was 22·43 grs. of chromic acid, in two cells, at 67°·3. The diffusion of

sulphuric acid at 63°·5, was 19·73 grs., which would give about 21 grs. of that acid at 67°·3.

Acetic Acid.—This acid cannot be determined accurately by the acidimetrical method, owing to the acetates of potash and soda being essentially alkaline to test-paper, like the carbonates of the same bases, although neutral in composition. The weight of carbonate of baryta dissolved by the acid was had recourse to.

Diffusion of acetate of water in ten days at 48°·8; two cells:—

	Grs.	Ratio.
From 2 per cent. solution	11·31	2
From 4 per cent. solution	22·02	3·83
From 8 per cent. solution	41·80	7·26

The diffusibility diminishes with the larger proportions of acid. This acid appears to be considerably less diffusive than sulphuric acid.

Sulphurous Acid.—Diffusion of sulphurous acid in ten days at 68°·1; two cells:—

	Grs.	Ratio.
From 1 per cent. solution	8·09	0·954
From 2 per cent. solution	16·96	2
From 4 per cent. solution	33·00	3·891
From 8 per cent. solution	66·38	7·827

This substance appears to be less diffusive than sulphuric acid at the same temperature; the diffusion of sulphurous acid at 68°·1 considerably resembles that of sulphuric acid at 49°·7.

Ammonia.—Diffusion of ammonia in 4·04 days, the time of hydrate of potash, at 63°·4; two cells:—

	Grs.	Ratio.
From 1 per cent. solution	4·93	1·029
From 2 per cent. solution	9·59	2
From 4 per cent. solution	19·72	4·117
From 8 per cent. solution	41·22	8·605

Ammonia appears to have a diffusibility approaching to that of hydrate of potash. It appears very similar to hydrocyanic acid at the same temperature; or to possess about three-fourths of the diffusibility of hydrochloric acid.

Alcohol.—Time of diffusion ten days. The quantity of alcohol diffused was determined by careful distillation. The density of the alcohol solutions in the phials was always made to exceed that of the water in the jars, by the addition of chloride of sodium to the former.

Diffusion of alcohol in ten days at 48°·7; two cells:—

From 2 per cent. solution	8·62
From 4 per cent. solution	16·12
From 8 per cent. solution	35·50

Alcohol does not appear to belong to the same class of diffusive substances as acetic acid, which might be expected from their similarity of composition, but possesses a considerably lower diffusibility.

Diffusion from 2 per cent. solutions in ten days:—

Acetate of water at 48°·8	11·51	100
Alcohol at 48°·7.....	8·62	74·9

The diffusion of alcohol approaches to one-half of that of sulphate of water at nearly the same temperature.

Alcohol may be substituted for water to dissolve certain salts, and at the same time be made an atmosphere into which these salts are allowed to diffuse. From experiments which have been commenced on this subject, it appears that the diffusion of hydrate of potash, iodide of potassium, chloride of calcium and others is about four times slower into alcohol of density 0·840 than into water. The salts likewise often exhibit the same relations in their diffusibility in alcohol, as in water, with some singular exceptions, such as chloride of mercury.

Nitrate of Baryta.—The time of diffusion of this and the two following nitrates was 11·43 days*. The salt diffused was precipitated by sulphuric acid, and calculated from the weight of the sulphate of baryta formed.

Diffusion of nitrate of baryta in 11·43 days at 64°·1; two cells:—

	Grs.	Ratio.
From 1 per cent. solution	7·72	1·026
From 2 per cent. solution	15·04	2
From 4 per cent. solution	29·60	3·936
From 8 per cent. solution	54·50	7·247

The diffusion of nitrate of strontia almost coincides with that of the isomorphous nitrate of baryta at the same temperature.

Diffusion from 1 per cent. solutions at 51°·5 in 11·43 days:—

Nitrate of baryta	6·73	100
Nitrate of strontia	6·79	100·89

Nitrate of Lime.—The diffusate was evaporated to dryness with an excess of sulphuric acid, and the nitrate of lime, which is always supposed anhydrous, was estimated from the sulphate of lime produced.

Diffusion of nitrate of lime in 11·43 days at 64°·1; two cells:—

	Grs.	Ratio.
From 1 per cent. solution	7·66	1·021
From 2 per cent. solution	15·01	2
From 4 per cent. solution	29·04	3·872
From 8 per cent. solution	55·10	7·334

The results throughout for this salt are almost identical with those of nitrate of baryta, although these two salts differ greatly in solubility, and in one being a hydrated, and the other an anhydrous salt.

Acetates of Lead and Baryta.—Diffused for 16·166 days; the time chosen before for sulphate of magnesia, with seven days for

* This time is to that of sulphate of magnesia (16·166 days) as the square root of 8 is to the square root of 16; but does not appear to express the true relation between these salts.

chloride of sodium. These salts were diffused into water slightly acidulated with acetic acid.

Diffusion of 1 per cent. solutions in 16·166 days; two cells:—

Acetate of baryta at 53°·5	7·50	100
Acetate of lead at 53°·1	7·84	104·53

Here, of two isomorphous salts, that of greatest atomic weight sensibly exceeds the other in diffusibility.

Chlorides of Barium and Strontium.—The diffusion of these salts being manifestly more rapid than that of the chloride of calcium, a shorter time was tried, which is to seven days, the time of chloride of sodium, as the square root of 3 to the square root of 4·5.

Diffusion of chloride of barium in 8·57 days at 63°; two cells:—

	Grs.	Ratio.
From 1 per cent. solution	6·32	1·047
From 2 per cent. solution	12·07	2
From 4 per cent. solution	23·96	3·970
From 8 per cent. solution	45·92	7·608

Diffusion of chloride of strontium in 8·57 days at 63°; 2 cells:—

	Grs.	Ratio.
From 1 per cent. solution	6·09	1·045
From 2 per cent. solution	11·66	2
From 4 per cent. solution	23·56	4·041
From 8 per cent. solution	44·46	7·626

Both the diffusates and ratios in the preceding table correspond closely with those of chloride of barium.

Chloride of Calcium.—The time for this and all the following magnesian chlorides and nitrates was 11·43 days.

Diffusion of chloride of calcium in 11·43 days at 63°·8; two cells:—

	Grs.	Ratio.
From 1 per cent. solution	7·92	1·032
From 2 per cent. solution	15·35	2
From 4 per cent. solution	30·78	4·010
From 8 per cent. solution	61·56	8·021

On comparing solutions of chloride of calcium and nitrate of lime, it appears that the correspondence between the 1 and 2 per cent. solutions is sufficiently close, but that in the 4 and 8 per cent. the salts diverge, as happens also with hydrochloric and nitric acids themselves. The nitrate in both cases falls off, while the chloride sustains throughout the high diffusibility of the lower proportions.

Comparing certain other salts with chloride of calcium diffused at the same temperature, 50°·8, the following are the results:—

Chloride of calcium	6·51	100
Chloride of manganese	6·63	101·85
Nitrate of magnesia	6·49	99·69
Nitrate of copper	6·44	98·92

The following additional magnesian chlorides do not exhibit so close a correspondence as the preceding:—

Chloride of calcium	6·51	100
Chloride of zinc	6·29	96·61
Chloride of magnesium	6·17	94·77
Protosulphate of iron	6·15	94·73
Chloride of copper	6·06	93·08

Sesquichloride of Iron.—A series of observations was made upon the diffusion of the different proportions of this salt from 1 to 8 per cent., but in all of them decomposition was determined by the diffusion, with turbidity also in the solution phial except in the 8 per cent. solution.

The mean diffusion from the 8 per cent. solution, at 63°·3, was 55·88 grs. of sesquichloride of iron, with 6·66 grs. of free hydrochloric acid, in two cells. It appears from this that perchloride of iron approaches the chloride of calcium in diffusibility. That the proto- and persalts of the magnesian metals should have a similar rate of diffusion, is not unlikely from other analogies which they exhibit.

Sulphates of Magnesia and Zinc.—The time chosen for the diffusion of these salts, namely, 16·166 days, is a multiple by 2 of the time of sulphate of potash, and by 4 of the time of hydrate of potash. The diffusate was evaporated to dryness and weighed.

Diffusion of sulphate of magnesia in 16·16 days at 65°·4; two cells:—

	Grs.	Ratio.
From 1 per cent. solution	7·31	1·144
From 2 per cent. solution	12·79	2
From 4 per cent. solution	23·46	3·671
From 8 per cent. solution	42·82	6·701
From 8 per cent. solution at 62°·8..	42·66	1
From 16 per cent. solution at 62°·8..	75·06	1·759
From 24 per cent. solution at 62°·8..	102·04	2·340

Diffusion of sulphate of zinc in 16·16 days at 65°·4; two cells:—

	Grs.	Ratio.
From 1 per cent. solution	6·67	1·091
From 2 per cent. solution	12·22	2
From 4 per cent. solution	23·12	3·784
From 8 per cent. solution	42·26	6·916
From 8 per cent. solution at 62°·8..	39·62	1
From 16 per cent. solution at 62°·8..	74·40	1·878
From 24 per cent. solution at 62°·8..	101·42	2·560

It is remarked that the diffusion of these two isomorphous salts, sulphate of magnesia and sulphate of zinc, differs so much, in the 1 per cent. solution, as 8·75 per cent. This, however, is considered to be an accidental error, the disturbances from changes of temperature and other causes of dispersion being in direct proportion to the duration of the experiment, and therefore much increased with long times; while the 1 per cent. solution also, from its low density, is the proportion most exposed to such errors. The sulphate of zinc appears to be the truest throughout, in its diffusion, of these two

salts. The approach to equality becomes close in the 4 per cent. and larger proportions of salt, particularly with the unusually high proportions of 16 and 24 per cent., which were observed in these salts. The diffusion of both salts falls off remarkably in the higher proportions. The result of the comparison of these two magnesian sulphates is no doubt favourable to the similarity of diffusion of isomorphous salts.

Sulphate of Alumina.—The time of diffusion was the same as that for sulphate of magnesia.

Diffusion of sulphate of alumina in 16·166 days at 65°·4; two cells:—

	Grs.	Ratio.
From 1 per cent. solution	5·48	1·074
From 2 per cent. solution	10·21	2
From 4 per cent. solution	19·28	3·780
From 8 per cent. solution	33·52	6·572

The diffusion of sulphate of alumina is very sensibly less than that of sulphate of zinc at the same temperature.

Nitrates of Silver and Soda and Chloride of Sodium.—Time of diffusion seven days.

Diffusion of nitrate of silver for seven days at 63°·4; two cells:—

	Grs.	Ratio.
From 2 per cent. solution	13·61	2
From 4 per cent. solution	26·34	3·87
From 8 per cent. solution	51·88	7·62

Diffusion of chloride of sodium and nitrate of soda in seven days, both at 63°·4; two cells:—

Chloride of sodium, 2 per cent. ..	12·37	100
Nitrate of soda, 2 per cent.....	12·35	99·83
Chloride of sodium, 4 per cent. ..	24·96	100
Nitrate of soda, 4 per cent.....	23·58	94·48
Chloride of sodium, 8 per cent. ..	48·44	100
Nitrate of soda, 8 per cent.....	47·74	98·55

As usual the chloride is slightly more rapid in its diffusion than the nitrate.

Chlorides, Iodides and Bromides of Potassium and Sodium.—Time of diffusion 5·71 days. The salt diffused was treated with nitrate of silver, and the chloride of silver weighed.

Diffusion of chloride of potassium in 5·71 days at 62°; two cells:—

	Grs.	Ratio.
From 1 per cent. solution	6·69	1·005
From 2 per cent. solution	13·32	2
From 4 per cent. solution	25·94	3·895
From 8 per cent. solution	53·64	8·054

The ratios are in remarkably close accordance with the proportions of salt diffused.

The times 5·71 and seven days chosen for the chloride of potassium and sodium, it will be observed, are as the square roots of 2 and 3. A certain deviation from this ratio of the times of equal

diffusion, appears on comparing the experimental results obtained at present for these salts.

The following is the result of the diffusion of three isomorphous salts of potassium.

Diffusion of 2 per cent. solutions in 5·716 days, at 59°·8 :—

	Grs.	Ratio.
Chloride of potassium	12·24	100
Bromide of potassium	12·46	101·80
Iodide of potassium	12·51	102·21
Mean.....	12·40	

The corresponding salts of sodium were also compared.

Diffusion of 2 per cent. solutions for seven days :—

	Grs.	Ratio.
Chloride of sodium at 60°	12·14	100
Bromide of sodium at 59°·8	11·93	98·27
Iodide of sodium at 59°·8	12·18	100·33
Mean.....	12·08	

In both groups there is a near approach to equality of diffusion. The times for the salts of the two bases being in the empirical proportion of the square roots of 2 and 3, the mean diffusates also approach pretty closely.

Bicarbonates of Potash, Ammonia and Soda.—Time of diffusion 8·083 days, or double that of hydrate of potash. The water of the jars was partially charged with carbonic acid gas, to prevent the decomposition of the bicarbonates in the act of diffusion.

Diffusion of bicarbonate of potash in 8·08 days at 68°·2; two cells :—

	Grs.	Ratio.
From 1 per cent. solution	7·23	1·029
From 2 per cent. solution	14·05	2
From 4 per cent. solution	26·72	3·806
From 8 per cent. solution	52·01	7·408

Diffusion of bicarbonate of ammonia in 8·08 days at 68°·2; two cells :—

	Grs.	Ratio.
From 1 per cent. solution	6·91	1·013
From 2 per cent. solution	13·65	2
From 4 per cent. solution	27·00	3·959
From 8 per cent. solution	50·10	7·346

The amount and progression of the diffusion of this salt correspond well, for all the proportions diffused, with the preceding isomorphous bicarbonate of potash.

Diffusion of bicarbonate of soda in 9·87 days at 68°·1 ; two cells :—

	Grs.	Ratio.
From 1 per cent. solution	7·31	1·059
From 2 per cent. solution	13·81	2
From 4 per cent. solution	26·70	3·869
From 8 per cent. solution	52·38	7·590

A remarkable approach to equality in the diffusion of the bicarbonates of potash and soda, in the times chosen, is observed equally in all the proportions of salt from 1 to 8 per cent.

The times chosen for the bicarbonates of potash and ammonia is to that of the bicarbonate of soda, as the square root of 2 to the square root of 3, and the remarkable agreement observed in the diffusion of these salts gives support therefore to that relation. In alluding to this relation, it is, however, added that the carbonates of potash and soda deviate from it in a sensible degree, and the hydrates of potash and soda very considerably; so that if the relation has a real foundation, it must be masked in the salts last named by differences existing between them in certain properties, the discovery and investigation of which is of the last importance for the theory of liquid diffusion.

Hydrochlorates of Morphine and Strychnine.—Time of diffusion 11·43 days. The quantity diffused was determined from the chlorine, which was precipitated as chloride of silver in an acid solution.

These two analogous salts appear to approach very closely in diffusibility.

Diffusion from 2 per cent. solutions at 64°·1; two cells:—

Hydrochlorate of morphine.....	11·60	100
Hydrochlorate of strychnine	11·49	99·05

The diffusion of these salts of organic bases in 11·43 days, is exceeded by the diffusion of chloride of ammonium or potassium in 5·71 days, or half the former time. The vegeto-alkalies appear thus to be divided from ammonia and potash.—*Phil. Trans.*, Part II. 1850.

Further Experiments on the Pancreatic Juice of the Dog.

By J. L. Lassaigne.

We know, from the interesting experiments of MM. Bernard and Barreswil, that the pancreatic juice possesses the remarkable property of forming an emulsion with fatty bodies, either vegetable or animal, and of transforming them into fatty acids and glycerine, at the temperature of from 95° to 100° F.

M. Bernard, in subsequently repeating, at the school of Alfort, along with M. Colin, the process by the aid of which he obtained the pancreatic fluid from animals, remitted to M. Lassaigne a portion of this juice, which he had extracted himself from a dog of middle size.

The experiments to which he submitted it, allow him to add some facts to those already known, and of which the principal may be stated in the following propositions:—

1. The action of the pancreatic juice upon oils is produced even at the temperature of 53° to 60° F. in some hours. In fact, on moistening several points of blue litmus-paper with the emulsion produced by the olive oil and pancreatic juice, the moistened portions of the blue paper reddened shortly, from the circumference to

the centre, on exposing to the air; and to produce this effect, it was not found necessary to leave the mixture during twelve or fourteen hours at the temperature of the bodies of mammalia, as has been advanced by the authors quoted above.

2. The mixture of the pancreatic juice and oil becomes acid at ordinary temperatures, as the author has ascertained after an experiment of similar duration.

3. This acidification is produced in oxygen, air, hydrogen, nitrogen and carbonic oxide gases; the air does not seem to participate in this singular change, which is perhaps due to a force of the same nature as that designated by Berzelius "catalytic force," to explain certain reactions in organs and inorganic chemistry.

4. The pancreatic juice can preserve its alkalinity and property of acting on oil for several days.

5. Under the same circumstances in which the oil is modified by this fluid, sugar and gum undergo no alteration, a circumstance which points out the speciality of the action which it exercises on fatty bodies.—*Journ. de Pharm.*, March 1851; and *Monthly Journal of Medical Science*, May 1851.

On the Modifications of the Oxide of Tin. *By* G. C. Wittstein.

The author thinks that the cause of the difference between the insoluble and soluble modifications of the oxide of tin is owing to a difference in the state of cohesion. He found that the soluble oxide of tin presents an amorphous appearance under the microscope, whilst the insoluble is constantly crystalline. Even after half an hour's boiling, the precipitate from perchloride of tin by ammonia distinctly exhibits a crystalline structure.—*Repert. de Pharm.*, v. p. 313.

On the Action of the Chloride of Cyanogen upon Wood-Spirit. *By* M. Echevarria.

When a current of chloride of cyanogen is passed into wood-spirit to which a little water has been added, no reaction is apparent so long as the liquid is not saturated; but when it has reached the point of saturation, a most lively reaction suddenly ensues, the liquid begins to boil, becomes turbid, and deposits chloride of ammonium.

After having separated this salt by filtration, I distilled the liquid, in order to separate the greater portion of the wood-spirit and other volatile products. In this operation a further quantity of chloride of ammonium is deposited, which is separated by filtration, and the distillation resumed. When the boiling-point has attained 284° F., the receiver is changed, and the distillation continued until the temperature of the thick black liquid in the retort has risen to 356°–374°. Beyond this point the liquid which passes is highly coloured.

By the next day the liquid in the receiver has deposited a considerable quantity of perfectly-transparent crystals, which it suffices

to press between filtering-paper to obtain perfectly pure. These crystals are urethylane, a substance which was first obtained by M. Dumas in the reaction of ammonia upon methylo-chloroxy-carbonic æther. The crystals are rhomboidal prisms, are not deliquescent; they melt between 126° and 131° F., and solidify at 131° when they are perfectly dry, but the least trace of moisture causes the point of solidification to descend to 122°. The melted liquid boils and volatilizes without decomposition at 351°. The density of the vapour of urethylane is 2·62, which corresponds to 4 vols.

Urethylane is very soluble in water; it dissolves less readily in alcohol, and still less in æther. 100 parts of water at 52° dissolve 217 parts of urethylane, whilst 100 parts of alcohol at 59° dissolve only 73 parts.

Sulphuric acid diluted with its weight of water decomposes urethylane, on the application of heat, into carbonic acid, wood-spirit and sulphate of ammonia—

$$C^4\,H^5\,NO^4 + SHO^4 + H^2\,O^2 = NH^3\,SHO^4 + C^2\,H^4\,O^2 + C^2\,O^4.$$

When the sulphuric acid is more concentrated, it acts upon the wood-spirit formed, the liquid blackens, and disengages sulphurous acid and inflammable gases.

Potash resolves urethylane into wood-spirit, ammonia and carbonic acid, which remains combined with the alkali.

The formation of urethylane in the reaction of chloride of cyanogen upon wood-spirit is satisfactorily explained by the following equation:—

$$C^2\,NCl + C^4\,H^4\,O^2 + H^2\,O^2 = C^4\,H^5\,NO^4 + HCl.$$

With respect to the ammonia which is simultaneously formed, it evidently results from the complete decomposition of the chloride of cyanogen by the molecule of water of the wood-spirit, $C^2\,H^3\,O$, HO, or by the water which is added to facilitate the reaction; it appeared probable that among the accessory products would be found a small quantity of methylo-carbonic æther, but I could not succeed in isolating it, nor could I detect any disengagement of methylo-muriatic æther.—*Comptes Rendus*, April 21, 1851.

Alloys of Silver and Copper. *By* M. Levol.

According to the author, the French coins, which should contain in 1000 parts 900 silver, differ in pieces from the same mixture as much as 3·14 parts in 1000 in the quantity of silver. In endeavouring to ascertain the cause of this difference, he found that there exists only *one* true chemical compound of silver and copper. This compound corresponds to the formula $Ag^3\,Cu^4$; all the other proportions give, on being melted, according to circumstances, more or less dissimilar mixtures of the above compound with copper or with silver. M. Levol advises, in order to obtain coins having exactly the same composition, that the above proportions be adopted for forming the alloy.—*Journ. de Pharm.*, xvii. p. 111.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Manufacture of Smalt. *By* C. Tomlinson.

This branch of manufacture is altogether foreign; and the chief material for it is almost entirely obtained from two small districts, one in Saxony, on the borders of Bohemia (visited by the author in the autumn of 1847), and the other in Norway.

The use of the ore from which smalt is manufactured (termed by the miners of Schneeberg *cobalt*) was discovered by one Christopher Schurer, a glass-maker at Neudeck. He first collected some of this Schneeberg ore, and tried it in his glass furnace, when he found, to his delight, that it communicated to glass a beautiful blue colour. This was about the year 1540, or perhaps earlier. Schurer made many trials of the new material, and at length succeeded in making of this blue glass *an enamel colour*, well adapted to the use of the potter. This colour found its way to Nuremberg, and at length to Holland, where it was highly appreciated by the Dutch artists. They sought out the humble glass-maker of Neudeck, and invited him, by large promises, to reveal his secret. He took up his residence for a time in Magdeburg, and had the ores of Schneeberg conveyed thither for the purposes of his manufacture. But he afterwards returned to Neudeck, and constructed a hand-mill for grinding his glass to powder, and afterwards another, which was driven by water. Meanwhile the Dutch had become expert in the preparation of the colour, so that they obtained from 100*s.* to 120*s.* per cwt. for it, while the price in Saxony was only 22*s.* 6*d.* per cwt. At a later period, therefore, the Elector of Saxony had to invite the colour-makers of Holland to teach their methods to his people; after which colour mills rapidly increased in the neighbourhood of the cobalt mines.

Thus for a very long period this beautiful colour continued to be manufactured from a mineral whose composition was unknown. It was not till the year 1733 that the Swedish chemist Brandt obtained from this ore the metal which he called *cobalt*, and proved that the colouring matter is the protoxide. In 1780 Bergman confirmed and extended Brandt's results; and in 1800 the subject was taken up by the School of Mines at Paris, and investigations were also carried on by Thénard and Proust.

Metallic cobalt is a brittle metal, of a reddish-gray colour; it fuses with difficulty, and has a magnetic character. This metal has not been applied to any useful purpose in the arts, and the interest attaching to it is purely scientific. The native combinations of cobalt are the oxide, and compounds of the metal with iron, nickel, arsenic and sulphur.

To obtain the oxide in a state of tolerable purity requires much careful and laborious manipulation, varying somewhat according to the nature of the ore. The first process is *picking*, by which stony fragments are removed, and the ores are separated into different

qualities; the richest being set aside for roasting, with little or no previous preparation, and those containing nickel being reserved for special treatment. The larger bulk of the picked ore is however subjected to the next process, which is *stamping* in a stamp-mill. Here a cam, or tappet-wheel, lifts up a number of pestles of pine-wood, shod with lumps of cast iron, and, suddenly releasing them, allows them to fall by their own weight upon the ore, which is distributed in chests beneath. The stamp-troughs are furnished with a stream of water, which washes out the pounded ore, and carries it down an inclined plane, where the sand and earthy matters, being much lighter than the metallic oxides, are carried furthest by the action of the stream, and are easily separated from the heavy and valuable particles. The ore thus washed is next *roasted* in a reverberatory furnace, provided with chambers for receiving and condensing the arsenic. The condensing tube is upwards of 100 feet in length, or a shorter tube is connected with chambers of several stories, where the arsenic (an important article in commerce) is collected by men wearing a dress fitting tightly in every part, a helmet with goggles for the eyes, and a wet bandage or sponge tied over the mouth and nostrils. They are still further fortified for their dangerous occupation by drinking a glass or two of olive oil. Their food also is regulated, and consists chiefly of vegetables, with abundance of butter. This is the system adopted in Silesia, at Reichenstein and Altenberg, where large quantities of arsenious acid, realgar and orpiment are manufactured from arsenical pyrites.

In the roasting of cobalt, the ore is wetted and spread over the sole of the reverberatory furnace, in a layer 5 or 6 inches deep; it is then cautiously heated for six hours, during which time abundant fumes are produced, consisting chiefly of vapour of water and arsenious and sulphurous acids; and the heat is then increased, and continued for sixteen, eighteen or twenty-one hours, the ore being disturbed with a rake, to bring all parts under the action of the flame and of the air. When the ore becomes red-hot, the operation ends; the ore is then withdrawn, and the furnace allowed to cool before a fresh charge is put in. The sand which was separated in the dressing is sometimes mingled, in certain proportions, with the ore in the roasting; and the product thus obtained is the zaffre or saffre of commerce, a crude product. *Smalt*, on the contrary, is a valuable and carefully-prepared vitreous compound, a rich blue glass in fact, to be afterwards reduced to powder, and elaborated in the manner now to be described. Glass is well known to be a compound of silica and an alkali; but this compound is not very stable. If we reduce a piece of glass to powder by grinding in a mortar, a considerable quantity of alkali can be washed out; and even by moistening pounded glass with water, a piece of turmeric paper will detect the presence of free alkali. Silica and potash, both very carefully prepared, calcined, sifted, and preserved from moisture, are mixed with oxide of cobalt, to form smalt, the proportions varying according to the commercial variety of the article required.

The ingredients are intimately mixed in a wooden trough, 2 feet

deep; and then they are transferred to the melting pots, which are built up in a furnace heated to the proper temperature, each pot being first charged with an inferior blue glass in powder, called *eschel*, the effect of which is to give an interior vitreous lining to the pots. The smalt mixture is poured into the pots by means of iron ladles with long handles, and in about eight hours it fuses, and a vitreous crust is formed on the surface; this is broken through, and the mixture stirred by means of an iron tool, made red-hot for the purpose. When the pots appear at a white heat, their contents are quite fluid, and the chemical combination of the materials has been effected.

When the glass attaches itself to the workman's rod, and can be drawn out into threads, it is ready for pouring; but it must first be carefully freed from two impurities, which interfere with the very dark homogeneous blue colour which the glass ought now to present. These are, first, *glass gall* or *sandiver*, which forms as a scum on the surface, and can therefore be skimmed off; and secondly, the metallic impurities of the oxide, which sink to the bottom, but are sometimes met with in diffused globules throughout the lower portion of the glass pot. This sediment is of variable composition, but may contain cobalt, nickel, iron, arsenic, bismuth, and even silver. It is known in commerce by the name of *speiss*.

The pure blue glass is next taken from the glass pot in iron ladles; and as the object of subsequent processes is to reduce the glass to powder, that object is facilitated by emptying the ladles into vessels of water, the water being constantly renewed. The glass being at a red-heat when it first comes in contact with the water, is thus rendered, like Prince Rupert's drops, excessively brittle, granular, and easy to pulverize. When the glass pot is half empty, the workman examines the contents of his ladle to see if any speiss is there; if so, he manages to separate it from the blue glass by skilful pouring. All the glass pots are thus emptied before a fresh charge is given to any one of them; for so great is the reduction of temperature in charging three or four pots, that the contents of the others would become solidified or too pasty to be ladled. The charging of the six pots reduces the furnace to a brownish-red heat; and an hour and a half is required to get it up again to the proper temperature, which is that of an ordinary glass furnace.

The next process in the manufacture of smalts is the apparently simple one of reducing the blue glass to powder. But if we try the experiment of grinding to powder a portion of blue glass, we shall find that the substance, which by transmitted light had appeared so beautiful, is reduced in its disintegrated state to a light dingy powder; yet who can doubt that the same amount of colouring matter is present in the powder as in the glass? There are therefore difficulties to be overcome in converting a sheet of blue cobalt glass into a powder of an intensely blue colour, and in obtaining all those shades and varieties of blue which are found in our manufactures. The processes are as follow:—The blue glass is first crushed in the dry state at a stamping-mill, then sifted to the size of ordinary sand, and this sand is afterwards ground in a mill between horizontal

granite stones, in quantities varying from $1\frac{1}{2}$ to 2 cwt. at a time. It is wetted with a little water, and the grinding is continued from four to six hours. The powder thus produced is then transferred to large vats full of water, and in the course of a very few minutes a separation of particles takes place in the powder. The heaviest, being those which are richest in cobalt, sink to the bottom; and this deposit constitutes one of the commercial varieties of smalts, known as *azure*, *coarse blue* or *streublau*.

The water which holds the finer particles of the powdered blue glass in suspension is drawn off into other vats, where it is allowed to subside for three-quarters of an hour or more, according to the variety of smalt intended to be produced; this second deposit is called *farbe*, the German word for *colour*. The water drawn off from this second deposit is poured into vats, and allowed to remain for an indefinite time; and its deposit is called *eschel*, or *blue sand*. But the colours thus obtained are all again subjected to the action of water before they are fit for the market. Each deposit is agitated in tubs abundantly supplied with water, and is again allowed to subside, while any floating impurities are removed with a sieve. The water then drawn off is treated as in the former case, and the various kinds of subsidence form different varieties of colour.

The glass of cobalt appears to be a mixture of the less fusible silicates, in which *cobalt* prevails, and which resist most perfectly the action of the water; and of the more fusible silicates, in which *potash* prevails, and which are more susceptible of the action of water. The former silicates constitute the *azure*, or coarse blue; and the latter are partially decomposed by water, which subtracts a subsilicate of potash, and leaves a supersilicate of potash in a minutely divided state. *Farbe* owes its tints to the subtraction of potash; and *eschel* contains more silica, and less potash and cobalt, than the other varieties.

The beauty of smalt is said to be heightened by what may be called accidental causes,—the presence of 4 or 5 per cent. of arsenic and arsenious acids; from 6 to 9 per cent. of phosphoric acid; and minute particles of zinc, tin, antimony and nitre. On the other hand, it is deteriorated by the presence of nickel, lead, iron beyond 10 per cent., bismuth, borax, soda, the alkaline earths, alumina, felspar, fluorspar and sulphur.

The precipitates of smalt dry into hard masses, which are crushed by mallets, then passed between cylinders, and sifted in fine sieves; the sieves are enclosed within a wooden case, and are set in motion by machinery. The azure is next dried in a hot room, under the tiled floor of which passes a winding flue. A number of shallow wooden troughs are arranged in this hot room, and the smalt is placed therein, and is stirred up from time to time with a rake. When sufficiently dry, it is taken to another room, where it is subjected to a final sifting, and the manufacture is complete. It is then slightly moistened, to prevent waste, and packed in small casks containing half a hundred weight each, and marked with the name of the shade.—*Proceedings of the Society of Arts.*

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

V. *On some Compounds of the Radicals* ($C^6 H^5$) R^n. *By* Dr. Hlasiwetz.

The author some time ago examined the oil of assafœtida, and found it to consist of a higher and of a lower sulphuret of the hydrocarbon $C^{12} H^{11}$, viz. $n(C^{12} H^{11} S^2) + m(C^{12} H^{11} S)$. Under certain circumstances, 1 atom of hydrogen separates from this hydrocarbon, and there is formed $2(C^6 H^5)$, which unites as such with sulphocyanogen, forming oil of mustard; it is the radical which is known by the name of allyle. This radical is the only one of five of the same atomic constitution whose sulphur and sulphocyanogen compounds are satisfactorily known; of the others, the oxygen, and in some cases also the chlorine compounds, have been prepared and examined, but not so the sulphurets and sulphocyanides. The object of the author's investigation was to discover the supposed relation between these bodies.

The substances under consideration have all the radical $C^6 H^5$, or a hydrocarbon double that. They are,—1st, the allyle compounds; 2nd, acetone, $C^6 H^5 O + HO$; 3rd, the oxide of mesityle, $C^6 H^5 O$; 4th, metacetone, $C^6 H^5 O$; 5th, the carbohydrates, $C^{12} H^{10} O^{10}$; and 6th, lactic acid, $C^{12} H^{10} O^{10}$.

The products of oxidation of almost all these bodies are known; they are generally acetic, formic and oxalic acids; metacetone gives metacetonic acid; some carbohydrates even furnish butyric acid, and the oil of assafœtida itself yields valerianic acid.

By oxidation with chromic acid, the author obtained from oil of mustard, acetic acid in abundance, but only a slight trace of metacetonic acid, sufficient to prove it qualitatively. Oxidized with nitric acid, a somewhat large amount of formic acid is formed; oxalic acid is left in the residue. The mode of oxidizing was the same as that which the author described in his former paper on the oil of assafœtida. The acetate of silver appeared in verruceous crystalline scales, consisting of fine soft needles, which became somewhat black by exposure to light. Analysis gave—

Carbon	14·5	4 =	24	14·3
Hydrogen	1·7	3	3	1·8
Oxygen	..	5	24	14·5
Oxide of silver	..	1	116	69·4

For the production of large quantities of metacetonic acid, both chromic acid, and especially nitric acid, appear to have too violent an action; metacetonic and formic acids seem to be produced. The products of oxidation of oil of mustard correspond with the view of the constitution of the oil of assafœtida insofar as only such acids are formed as contain 6 or less equivs. of carbon, whilst in the case of the latter oil, valerianic acid is likewise readily formed.

Acetone, $C^6 H^6 O^2$, *gives sulphocarbaminate of the sulphuret of acetonyle and sulphocyanide of acetonyle.* When pure acetone is mixed with an equal bulk of sulphuret of carbon and about twice the amount of ammonia, there are formed in the lower yellow layer of liquid, in the course of two or three days, laminar ice-like crystals, which again disappear after some time; whilst larger and more compact crystals of a yellow colour separate, and frequently grow to a considerable size. If they are removed after ten or twelve days from the mother-liquor and the second dark red stratum of liquid, which contains sulphuret of ammonium, washed with water and dried between bibulous paper, they appear of an amber or orange colour, and are generally opake; when reduced to powder, the colour is of a lighter yellow, and a faint odour, calling to mind acetone and sulphuretted hydrogen, is diffused, which becomes stronger on keeping, owing to a decomposition. They are insoluble in water. They dissolve in dilute muriatic acid only on boiling, with separation of a small quantity of sulphur. Alcohol takes up a large quantity on the application of heat, but with decomposition; æther dissolves but very little. Heated upon platinum foil, they melt quickly, and burn with a blue flame, diffusing an odour of sulphurous and prussic acid. Dried *in vacuo*, they furnished on analysis—

	I.	II.			
Carbon.....	45·54	45·74	30 =	180	45·91
Hydrogen	7·13	7·00	26	26	6·63.
Nitrogen	10·69	..	3	42	10·73
Sulphur	37·23	..	9	144	36·73

These numbers correspond to the formula $2(C^6 H^6 S), (C^2 H^2 NS^3) + 2(C^6 H^6, CyS^2)$, *i. e.* the sulphocarbaminate of the sulphuret and the sulphocyanide of $C^6 H^6$, acetonyle. The presence of sulphocyanogen is readily proved. Caustic potash dissolves the crystals, and gives on boiling the odour of oxide of mesityle, and subsequently of ammonia; if the solution is saturated, before or after the boiling, with some muriatic acid, and perchloride of iron added, a strong reaction of sulphocyanogen immediately results. This compound is formed under the same conditions as the sulphocyanide of benzoyle examined by Quadrat. With bichloride of platinum it gives the following compounds:—

$C^{30} H^{26} N^3 S^9 + 3PtS^2$.—Cold alcoholic solutions of the bichloride of platinum and of the crystalline compound furnish, on being mixed, a precipitate which is somewhat soluble in alcohol, and is increased by the addition of a little water. It however takes some time before the whole is precipitated, and in general the portions

which separate towards the end are of a somewhat lighter colour. On the whole, the precipitate is of a brownish-yellow, and decidedly uncrystalline, even when it has separated from boiling alcohol. It may be dried at 212°; when heated, it first gives off an empyreumatic odour, and then one of sulphuretted hydrogen and sulphurous acid, and finally burns to pure platinum. Mixed with sulphocyanide of potassium and heated, no oil of mustard is produced. The analysis of this compound gave—

Carbon	22·84	30	= 180·0	22·97
Hydrogen	3·32	26	26·0	3·31
Nitrogen	5·48	3	42·0	5·35
Sulphur	..	15	240·0	30·78
Platinum	37·64	3	295·6	37·59

The mercury compound is readily obtained by precipitating an alcoholic solution of the crystals with a similar solution of corrosive sublimate. At first it forms a perfectly white powder, which on drying turns somewhat yellowish, is sparingly soluble in alcohol, and insoluble in water. On being mixed with perchloride of iron, especially on being warmed, it gives the reaction of sulphocyanogen. With the alkaline sulphocyanides it furnishes as little oil of mustard as the preceding salt. It contains, along with sulphuret of mercury, a considerable amount of protochloride of mercury, and blackens on being treated with potash. It furnished on analysis, after being dried at 212°,—

Carbon	2·94	30	= 180	3·03
Hydrogen	0·46	26	26	0·43
Nitrogen	..	3	42	0·70
Sulphur	9·87	36	576	9·70
Mercury	76·65	45	4500	75·84
Chlorine	9·83	18	609	10·30

In accordance with this the author advances the formula $(C^{30}\ H^{26}\ N^3\ S^3) + (27HgS, 18HgCl)$. Whilst the compound $2(C^6\ H^6\ S) + C^2\ H^2\ NS^3 + 2(C^6\ H^6, CyS^2)$ is resolved, on boiling with caustic potash, into oxide of mesityle, ammonia is disengaged. When the crystals are heated to their melting-point, two liquids distil over, which separate into two layers, precisely as if from a mixture of acetone, sulphuret of carbon and ammonia, from which they have originated. The inferior layer is pale yellow, and the presence of acetone and sulphuret of carbon is readily detected in it by the smell; the upper layer is dark red, and contains much sulphuret of ammonium. Almost simultaneously with the decomposition into these constituents, some fine, shining, white needles appear in the neck of the retort, which are inodorous, have an intensely bitter taste, and are equally soluble in alcohol, water and æther.

Acetonylamide and Sulphocyanide of Acetonyle.—When the crystals of the sulphocarbaminate of the sulphuret of acetonyle + sulphocyanide of acetonyle are boiled with alcohol, ammonia and car-

bonic acid are disengaged; and subsequently the solution is decomposed, gradually becoming darker until it has a brown-red colour, with formation of sulphuret of ammonium.

At the same time there collects at the bottom of the vessel on standing a small quantity of a new crystalline compound, which it is difficult to free from the colouring mother-liquor, and must be purified by repeated crystallization. The substance then appears white; it contains sulphocyanogen, and gives, when dried under the air-pump,—

Carbon	51·45	36 =	216	51·67
Hydrogen	9·00	36	36	8·61
Nitrogen	16·84	5	70	16·74
Sulphur	..	6	96	22·98

This composition corresponds to the formula $2(C^6 H^6, NH^2) + 3(C^6 H^5, CyS^2)$, according to which, from the sulphur compound of sulphocarbaminic acid, has originated an amide compound united with the same sulphocyanogen compound as in the original salt.

Experiments on the Oxide of Mesityle, $C^6 H^5 O$.—To convert the oxide of mesityle into a sulphur compound, its chlorine compound was sought to be prepared, according to Kane, by means of the pentachloride of phosphorus, in order that it might then be decomposed by sulphuret of potassium. But in this manner only a small amount was obtained. The preparation of the sulphurous product is far more successful when the sulphoxymesitylate of lime is distilled in the dry state with mono- or pentasulphuret of potassium. Even on triturating the two substances together, the mass becomes somewhat warm, and gives off an intense odour of garlic, which on further distillation is most disagreeably increased. The peculiar reaction begins between 248° and 266°, and requires, when once commenced, no further heating. When monosulphuret of potassium is used, the distillate is at first perfectly clear; the subsequent portion is somewhat turbid, but it dissolves in the first. It is not difficult to observe that even as long as the liquid remains clear, a second one passes over of a higher specific gravity, which mixes with the first; this appears to arise from a variable amount of sulphuretted hydrogen, which is disengaged in abundance during the entire operation. At a later period water passes over, which dissolves much of the compound, on which account the recipient must be changed in time.

When chloride of calcium is added to the mixed product thus obtained, a large amount is dissolved; when no more is taken up, the residual liquid is drawn off and rectified alone. The thick paste of chloride of calcium is then distilled in the water-bath, when a colourless oil passes over, which smells of onions and burns with a blue flame. Its composition is—

Carbon	46·72	46·60	18 =	108	46·75
Hydrogen	11·94	11·95	27	27	11·64
Oxygen	26·78	..	8	64	27·76
Sulphur	14·56	..	2	32	13·85

The oil which was no longer taken up by chloride of calcium most probably contains no oxygen. To remove the excess of sulphuretted hydrogen, it was shaken with dilute milk of lime, which may have somewhat decomposed it. Analysis gave 45·03 carbon, 10·67 hydrogen, 41·45 sulphur, and a remainder of 2·85 oxygen. The author assigns to this body the formula $C^6 H^6 S + HS$, which requires in 100 parts, 48·1 C, 9·3 H, 42·6 S.

The analyses of two oils of different preparations, collected whilst the distillate was still uniform, then washed with carbonate of soda to remove any free sulphuretted hydrogen, and dried over chloride of calcium, led to similar formulæ, which only differ by containing a greater or less amount of sulphuretted hydrogen. Thus the results A correspond to the formula $C^6 H^6 S + 2HS$, those under B to the formula $3(C^6 H^6 S + 2HS) + (C^6 H^6 S + HS)$:—

	A.			B.			
Carbon	39·17	6=36	39·13	41·53	24=144	41·02	
Hydrogen	8·99	8	8	8·69	9·17	31	31	8·83
Sulphur.....	..	3·	48	52·18	49·59	11	176	50·15

When the pentasulphuret of potassium is used for the preparation of these sulphurous oils, which are all characterized by an extremely disagreeable odour of garlic, there is formed, besides the very mobile colourless oil, upon raising the temperature, a yellow oil, which passes over along with much water, and which sinks to the bottom of the receiver. The colourless oil, which must be removed before any water makes its appearance, has nearly the same composition as the oil B; it contains 41·28 carbon and 8·60 hydrogen.

The heavy yellow oil, which has a more decided smell of onions, was used to prepare a compound with chloride of platinum, which is obtained when the spirituous solutions of the two substances are mixed, and the liquid immediately filtered from the dark red precipitate, consisting almost entirely of sulphuret of platinum, then a little water added till it begins to grow turbid, when the formation of a light yellow amorphous compound is assisted by warming on the water-bath. Washed with alcohol and dried at 212°, it gave on analysis—

Carbon.....	14·24	60 =	360·0	14·45
Hydrogen.....	1·96	50	50·0	2·00
Platinum	55·41	14	1379·8	55·41
Sulphur	16·55	26	416·0	16·50
Chlorine	11·84	8	284·0	11·64

leading to the formula $2(C^6 H^5 Cl), 3(PtCl) + 8(C^6 H^5 S, PtS) + 7PtS^2$.

The above-described oils may be deprived of sulphur by agitating them for a long time with caustic potash and peroxide of mercury. The penetrating garlic odour then almost entirely disappears.

The oil above described, for which the author proposes the formula $3(C^6 H^6) + S + HS + 8aq$, exhibited, after being distilled from the mixture of potash and mercury, the property of dissolving chlo-

ride of calcium, over which it was therefore rectified on the water-bath. It gave on analysis—

Carbon.....	46·23	48 =	288	46·82
Hydrogen.....	11·61	71	71	11·54
Oxygen	39·54	30	240	39·04
Sulphur.....	2·62	1	16	2·60

From the quantity of water, combined with which this oil distils off chloride of calcium, it appears that the compound $C^6 H^6 O$, *i. e.* the oxide of acetonyle, cannot exist without a large amount of water.

In the same manner as sulphur compounds of the kind above described are formed by distilling sulphoxymesitylate of lime with sulphuret of potassium, we should undoubtedly succeed in producing the corresponding compounds with phosphorus, cyanogen and amidogen, by employing phosphuret of calcium, cyanide of potassium, &c., and so completing the series of these compounds. A sulphocyanogen compound appears to be formed, for sulphoxymesitylate of lime and sulphocyanide of potassium furnish a distillate of an acrid penetrating odour, but entirely different from that of oil of mustard, which dissolves with milkiness in ammonia, and furnishes crystals on evaporating the solution.

Experiments with Metacetone, $C^6 H^5 O$.—The metacetone prepared by Gottlieb furnishes with sulphuret of carbon and ammonia no analogous compound to acetone. The crystals produced are sulphocarbaminate of the sulphuret of ammonium. Sulphuret of potassium and the sulphocyanide of potassium produce no decomposition having for result the formation of a sulphur or sulphocyanogen compound. The grayish-green precipitate which forms in an alcoholic solution of metacetone and perchloride of mercury furnishes no such compound on being heated with sulphocyanide of potassium.

Experiments with the Carbohydrates, $C^{12} H^{10} O^{10}$.—The experiments made with sugar and starch led to no result; they were distilled with sulphur, sulphuret of calcium, sulphuret of potassium, caustic lime and sulphur. A copious disengagement of sulphuretted hydrogen always resulted, whilst an empyreumatic liquid resembling metacetone and combustible gases passed over. No constant sulphur compounds could be produced in this manner.

The result of all these experiments, in reference to the question, whether, in the substitution of oxygen by sulphur or sulphocyanogen in the different hydrocarbons consisting of $C^6 H^5$, compounds are formed which are identical with those of allyle, is most decidedly negative. The compounds obtained in their stead are—

1. The combination of sulphocarbaminic acid with the sulphuret and sulphocyanide of acetonyle $= 2(C^6 H^6 S)$, $(C^2 H^2 NS^3) + 2(C^6 H^6, CyS^2)$.

2. Acetonylamide + sulphocyanide of acetonyle $= 2(C^6 H^6, NH^2) + 3(C^6 H^6 CyS^2)$.

3. The double salts with platinum and mercury, corresponding

to the first compounds, $=(C^{30}H^{26}N^3S^4)+3PtS^2$ and $(C^{30}H^{26}N^3S^9)+27HgS+18HgCl$.

4. The mono- and bisulphuret of acetonyle with sulphuretted hydrogen $=3(C^6H^6)+S+HS$, 8aq; C^6H^6S+HS(?); C^6H^6S+2HS; $3(C^6H^6S, 2HS)+(C^6H^6S, HS)$.

5. The oxide of acetonyle (hydrated) contaminated with sulphuret of acetonyle $=7(C^6H^6O)+(C^6H^6S)+23aq$.

6. Lastly, the double compound of the chloride and sulphuret of mesityle with the chloride and sulphuret of platinum $=2(C^6H^5Cl)$, $3(PtCl)+8(C^6HS, PtS)+7PtS^2$.

The only question still requiring an answer is, whether allyle exhibits any connexion through its oxygen compounds with those of the isomeric hydrocarbons. The oxide of allyle, the obtaining of which in a pure state is so difficult owing to its rapid oxidation, might possibly be the anhydrous aldehyde of metacetonic acid, and it was important to ascertain whether this oxidation would of itself proceed as far as metacetonic acid. In this respect the author found the oxide $AllO^2$ was frequently formed, and that this is not further altered, although, on the other hand, metacetonic acid is one of the products of oxidation of allyle. For instance, if oil of mustard be boiled several hours with a concentrated solution of caustic soda in an apparatus in which the vapours are constantly recondensed, the remainder of the oil, amounting to about a third of the quantity employed, acquires a totally different and milder smell, which is most distinct when the ammonia contained in the liquid is neutralized. By treatment with a warm solution of oxide of lead in potash, in case it still might contain a trace of sulphur, repeated washing with dilute sulphuric acid and water, and rectification, it is obtained pure; it is limpid, and has an odour resembling pickled fish. The residual mother-liquor contains traces of metacetonic acid, sulphuret of sodium and carbonate of soda. The ammonia which is formed from the cyanogen may be received in muriatic acid.

Oil of mustard and soda lime act violently on each other; the mixture becomes heated, and on distilling, after some time a colourless product is obtained, which has a strong ammoniacal odour, and of which a small part is taken up by water, a larger part by dilute sulphuric acid, whilst the remainder floats on the surface as a yellowish oil.

This oil, after it has been rectified, resembles greatly in its physical properties that obtained in the first experiment. Exactly the same salts are met with in the residual soda-lime as previously in the mother-liquor. The composition of this oil is as follows:—A is that obtained by boiling oil of mustard with a solution of caustic soda, and B that procured by treating the oil of mustard with soda-lime:—

	A.	B.			
Carbon.....	61·79	61·49	36 =	216	61·53
Hydrogen	8·56	9·04	31	31	8·82
Oxygen	29·65	29·47	13	104	29·65

This corresponds to the formula $6(C^6 H^5 O^2)HO$. Wertheim obtained numbers from his products closely corresponding to the formula $C^6 H^6 O^{1\frac{1}{2}}$, which therefore form in a certain measure a transition to this compound; this latter remains for a long time unaltered, whilst the former experienced a progressive increase in the amount of oxygen. The compound $C^6 H^5 O^2$ has likewise the property, in common with Wertheim's oils, of producing in a concentrated alcoholic solution of nitrate of silver crystals of a double salt having all the properties of the nitrate of silver and oxide of allyle.

As above mentioned, the distillate obtained in the reaction with soda-lime parts with a portion to dilute sulphuric acid, and only the small residue is the compound $C^6 H^5 O^2$. To obtain further information respecting it, the crude distillate was freed from ammonia under the air-pump over sulphuric acid, the residue mixed with very dilute sulphuric acid, and the separated oil distilled off. The acid liquid passed perfectly clear through a moistened filter, and gave, on being mixed with chloride of platinum, a yellow somewhat flocculent precipitate. This, after being washed, was removed from the filter and dried at 212°, at which temperature it puffs up and partially fuses, without being decomposed; if reduced to a powder, in this state it may be perfectly dried; on combustion, it turns black, and leaves 33·63 per cent. of porous platinum of a silver-white colour, as in the case of the platinum salt of thiosinnamine analysed by Will. The calculated amount however is only 30·62; but Will has stated, that if the solution of the thiosinnamine has not been previously saturated with muriatic acid gas, a much larger amount of platinum is always obtained.—*Proceedings of the Vienna Academy.*

√ *On the Absorption of Nitrogen from the Atmosphere by Plants.* *By* M. Ville.

The author sowed various kinds of seeds in a mixture of equal parts of sand and brickdust, which had been ignited for several days in a porcelain furnace. 5 per cent. of ash of the same kinds of plants as those that were to be cultivated were added to the mixture, and the whole closed air-tight in a bell-glass. The air was examined as to its amount of ammonia on its entrance and likewise on its exit. The amount of ammonia in the atmosphere is, when accidental sources are guarded against, scarcely determinable with much greater quantities of air than have hitherto been usually examined. The air was passed through the bell-glass by means of an aspirator, and was impregnated with 5–7 per cent. of carbonic acid. The author arrives, by his experiments, at the conclusion, that plants absorb nitrogen from the air, and use it for the formation of their nitrogenous products.—*Comptes Rendus*, xxxi. p. 578.

√ *On the Preparation of the Metallic Acids.* *By* A. Reynoso.

The facility with which the permanganate of potash parts with its oxygen led me to think it might be possible, by operating in the

presence of potash, to prepare certain salts of metallic acids, some of which had hitherto not been obtained in the dry way.

I first tried the action of a mixture of permanganate of potash and caustic potash upon a salt of the sesquioxide of chrome; the reaction was instantaneous at the ordinary temperature. On filtering, in order to separate the oxide of manganese produced, and destroying the permanganate of potash in excess by some organic body, paper for instance, a liquid is obtained which contains only chromate of potash with an excess of alkali. This reaction is so precise, that it may be employed to detect traces of chrome. For this purpose it is merely necessary to operate as above described upon the liquid under examination, and to ascertain in the liquid deprived of excess of alkali by acetic acid all the properties of the chromates. To the above character should be added the formation of perchromic acid by means of oxygenated water. The perchromic acid dissolves in æther, which it colours violet-blue if any be present. This test, which is as elegant as it is sensitive, is due to M. Barreswil.

The protosalts of antimony may likewise be oxidized, and that useful test for soda, antimoniate of potash, prepared in this manner. It suffices to precipitate the protosalt of antimony by potash, and to redissolve the precipitate in an excess of alkali, adding permanganate of potash until the liquid remains coloured: to remove the excess of permanganate of potash, a few drops of an alkaline solution of oxide of antimony may be added. If an organic substance is employed to destroy the excess of permanganate of potash, a portion of the manganese remains in solution in the potash, owing to the organic matter, which however would not be of any consequence, as the salt desired should be purified by crystallization. When the liquid has been thus decolorized, it is evaporated and set aside to cool; it deposits minute crystals of antimoniate of potash, which are washed until what passes contains neither chloride of potassium nor potash.

I have observed, that, in dissolving oxide of antimony in potash, it is advisable to pour the salt of antimony into the potash, for then the oxide of antimony in the nascent state dissolves readily in an excess of potash; whilst when the potash is poured into the protosalt of antimony, the oxide agglomerates, and no longer dissolves completely.

This method of preparing the antimoniate of potash has the advantage of furnishing in a brief space of time a reagent, the production of which was tedious, and so delicate that it was rarely obtained. The importance of a quick process for the preparation of this salt will be conceived if we bear in mind its ready decomposition. In fact, as shown by M. Fremy in his paper on the metallic acids, the crystalline antimoniate of potash in solution is converted after a certain time into the gummy antimoniate and biantimoniate of potash; so that there remains a mixture of biantimoniate, granular and gummy antimoniate, a mixture which, as it precipitates not merely salts of potash, but likewise all the soluble salts, might lead into

error, the more as this decomposition sometimes takes place in the course of twenty-four hours. However, M. Fremy states that he kept some granular antimoniate in solution for several months without detecting any decomposition.

Protosalts of tin, submitted to the same treatment, furnish stannate of potash.

With respect to the sesquioxide of iron and the deutoxide of copper, it would *à priori* be imagined that they would not be converted into ferric and cupric acids, as these acids are destroyed in the presence of finely-divided substances, such as the oxide of manganese, which would necessarily be formed in this reaction. The truth of this supposition was proved by experiment.

Lead passes into the state of peroxide, but this does not unite with the potash. Salts of bismuth gave no result.—*Comptes Rendus*, April 28, 1851.

√ *On Aspartic Acid from Malic Acid. By* Dr. J. Wolf.

The object of the author was to confirm by analysis Dessaignes' experiments of producing aspartic acid by heating bimalate of ammonia*. Some bimalate was retained in an oil-bath at a temperature of 338°–374° F. until there was no further appearance of aqueous vapour. The reddish-white mass was then exhausted with hot water until it became white, and parted with nothing further. A substance dissolves in this water, which separates on cooling as a fine powder remaining suspended in the liquid, but which can be immediately precipitated by the addition of an acid. It was several times dissolved in water, thrown down by an acid, washed, and then analysed. It gave 50·1 carbon, 4·1 hydrogen, 12·2 nitrogen, and 33·6 oxygen. Although the substance was not perfectly pure, it appears to be a compound corresponding to the imides. The formula $C^8 H^4 O^8 + NH^3 - 4HO = C^8 H^3 NO^4$ requires 49·5 C, 3·1 H, and 14·4 N.

The exhausted mass is now boiled for some time with muriatic or nitric acid, in which it dissolves. No oxidation takes place with the use of nitric acid. When the solution is no longer rendered turbid by the addition of water, the whole is evaporated on the water-bath to dryness to expel all nitric acid; otherwise the residue forms a gummy mass. This residue, which is very readily soluble in water, still contains some of the mineral acid employed, chemically combined; one-half is neutralized with ammonia, and then mixed with the other half, when the acid crystallizes out, which can be hastened by an addition of alcohol. Or the compound, dissolved in acid and evaporated to dryness, may be neutralized with lime, and the aspartate of lime precipitated by alcohol, when the nitrate remains dissolved. The lime-salt may then be decomposed by oxalic acid.

The acid thus prepared is somewhat difficult of solution in water, and still more so in alcohol. Its salts are for the most part soluble in water. The lime and baryta salts do not crystallize, but form on

* Chem. Gaz., vol. viii. p. 156.

evaporation a gummy mass, which when heated above 212° becomes brittle and fissured. The ammonia salt of the acid gives a bluish-white precipitate with a solution of copper. The silver salt is scarcely soluble in water, but very readily soluble in excess of ammonia. When the acid is not quite pure, a precipitate is obtained upon the addition of nitrate of silver only, which contains the impurities; by filtration and precipitation with ammonia, the silver salt is then obtained perfectly pure; it can be dried at 212°, but at 248° it begins to turn black. The acid is especially characterized by the circumstance, that on being evaporated perfectly to dryness with nitric or muriatic acid, it furnishes a very readily soluble compound in water, which contains the mineral acid employed in chemical combination. Moreover the analysis agrees perfectly with the composition of aspartic acid :—

Carbon	36·2	8 =	48	36·1
Hydrogen	5·6	7	7	5·3
Nitrogen	10·0	1	14	10·5
Oxygen	48·2	8	64	48·1

The baryta salt contained 37·6 per cent. of baryta, the formula $C^8 H^6 NO^7$, BaO requires 37·9. The silver salt left 61·0 and 62·0 per cent. of silver; the formula $C^8 H^5 NO^6$, 2AgO requires 61·7.—Liebig's *Annalen*, lxxv. p. 293.

On the Combinations of the Perchloride of Mercury with the Alkaloids. *By* F. Hinterberger.

Quinine and Perchloride of Mercury, $C^{20} H^{12} NO^2 + HCl$, HgCl. —The solution of quinine in alcohol rendered slightly acid with muriatic acid produces in an alcoholic solution of perchloride of mercury, after some time, a granular crystalline precipitate. When dilute alcohol is employed, the precipitate falls quickly, but less distinctly crystalline. It is sparingly soluble in alcohol, æther and water, and remains unaltered at 212°. It gave on analysis—

Carbon	35·60	36·00	20 =	120	35·93
Hydrogen	3·85	3·93	13	13	3·89
Mercury	30·08	29·66	1	100	29·94
Nitrogen	..	..	1	14	4·19
Chlorine	..	..	2	71	21·26
Oxygen	..	..	2	16	4·79

Cinchonine and Perchloride of Mercury, $C^{38} H^{22} N^2 O^2 + 2HCl$, 2HgCl.—Equal parts by weight of cinchonine and perchloride of mercury, dissolved separately in strong alcohol, a little muriatic acid added to the solution of the cinchonine, and the two solutions mixed, constantly stirring, furnish a paste of acicular crystals; these are brought upon a filter, and washed first with very strong alcohol, then with a large quantity of water, and finally with a mixture of æther and alcohol. The air-dried crystals can be completely dried without alteration on the water-bath. The compound is almost in-

soluble in cold water, moderately strong alcohol and æther, but pretty readily soluble in hot water and warm weak spirit. Cold concentrated muriatic acid dissolves it abundantly. On analysis it gave—

Carbon	35·42	35·40	35·69	..	38	=228	35·74
Hydrogen	3·80	3·86	3·82	..	24	24	3·76
Mercury	31·46	31·55	31·44	..	2	200	31·35
Chlorine.....	..	..	..	21·67	4	142	22·26
Nitrogen	..	..	..	..	2	28	4·39
Oxygen	..	..	..	..	2	16	2·50

Piperine and Perchloride of Mercury, $C^{70}\,H^{37}\,N^{2}\,O^{10} + HCl$, $2HgCl + 2HO$.—A solution of 1 part of piperine in strong alcohol, to which a little muriatic acid has been added, gives, when mixed with a spirituous solution of 2 parts of perchloride of mercury, after some days, yellowish crystals, which are washed with absolute alcohol. In the air and in the water-bath at 212° they turn darker yellow, but retain their lustre and their transparency. They are insoluble in water, very sparingly soluble in concentrated muriatic acid and cold alcohol, but more readily soluble in hot spirit. They furnished on analysis—

Carbon	46·96	46·55	70 =	420·0	47·17
Hydrogen.....	4·47	4·51	40	40·0	4·49
Mercury	22·33	22·37	2	200·0	22·46
Nitrogen	..	..	2	28·0	
Chlorine	..	..	3	106·5	
Oxygen.....	..	..	12	96·0	

Morphine and Perchloride of Mercury, $C^{34}\,H^{19}\,NO^{6} + HCl$, $4HgCl$.—An aqueous solution of muriate of morphine instantly gives with an aqueous solution of perchloride of mercury in excess a copious white crystalline precipitate. After some time, tufts of silky crystals separate from the filtered liquid. The white precipitate and these crystals are the same compound. If the crystalline precipitate originally obtained be dissolved in hot spirit, the greater portion separates on cooling in somewhat larger spangles. This compound is very sparingly soluble in cold water, alcohol and æther; concentrated muriatic acid dissolves it in large quantity at the ordinary temperature, from which solution it separates, on spontaneous evaporation in a closed space over caustic lime, in large colourless crystals, with a vitreous lustre. It furnished on analysis—

Carbon.....	23·54	23·50	..	34	=204·0	23·63
Hydrogen	2·33	2·36	..	20	20·0	2·32
Mercury	46·18	46·07	46·11	4	400·0	46·32
Chlorine	..	..	..	5	177·5	20·55
Nitrogen	..	..	..	1	14·0	1·62
Oxygen	..	..	..	6	48·0	5·56

Liebig's *Annalen*, lxxvii. p. 201.

✓ *On Liquid Phosphorus. By* J. Kallhofert.

The author dissolved phosphorus in sulphuret of carbon, covered the solution with a thin layer of distilled water, and the vessel with a glass plate. After somewhat more than nine months, the sulphuret of carbon had evaporated, but the phosphorus remained fluid. The author then exposed this fluid phosphorus for four months to the rays of the sun. The phosphorus below the layer of water was still perfectly fluid, and coated on the surface with a crystalline powder. It was now heated to boiling, and the vessel again exposed for four weeks to the sun. Neither solid nor red phosphorus was obtained. The fluid phosphorus, covered with water, was dipped into a freezing mixture; the phosphorus remained liquid beneath the ice.—*Jahrb. für Prakt. Pharm.*, xxi. p. 254.

✓ *On the Hydruret of Nitrated Benzoyle. By* M. Bertagnini.

The author has found that the oil of bitter almonds, when treated with a mixture of sulphuric and fuming nitric acid, furnishes a crystalline substance represented by the formula $C^{14}\,H^{5}\,(NO^{4})\,O^{2}$, which corresponds to the hydruret of benzoyle, in which 1 equiv. of hydrogen is replaced by 1 equiv. nitrous vapour.

This new substance reproduces the characteristic reactions of the primitive group; thus oxidizing agents convert it into $C^{14}\,H^{5}\,(NO^{4})$, *i. e.* nitrobenzoic acid identical with the acid of M. Mulder. Ammonia furnishes trinitrated nitrobenzamide, $C^{42}\,H^{15}\,(NO^{4})^{3}\,O^{4}$; hydrosulphuric acid gives the substance $C^{14}\,H^{5}\,(NO^{4})\,S^{2}$, which corresponds to the hydruret of the sulphobenzoyle of M. Laurent. —*Comptes Rendus*, May 5, 1851.

ANALYTICAL CHEMISTRY.

✓ *On the Analysis of some Metallic Alloys. By* C. Brunner.

The notice published by M. Brunner contains the following observations, which may be of service to the analytical chemist:—

Estimation of Copper.—In a very large number of cases the copper is separated from solutions containing it by sulphuretted hydrogen. As it is impossible to weigh directly the precipitated sulphuret of copper, it is usually redissolved in nitric acid, and the oxide of copper then precipitated by potash. The author describes a more ready and sure method, which consists in heating the sulphuret in a glass tube while a current of hydrogen is passed over it; it is then reduced to the state of subsulphuret, the weight of which is precisely equal to that of the oxide of copper corresponding to the same quantity of metal, ($Cu^{2}\,O^{2}$).

Estimation of Tin.—In general the tin in alloys is determined by

treating them with nitric acid, which dissolves the other metals, and leaves the tin in the state of insoluble stannic acid. But it frequently happens that some portion of the other metals remains inclosed in the stannic acid, and escapes the solvent action of the nitric acid. To avoid this inconvenience, the author recommends the following method:—The alloy, without its being requisite to reduce it to a very fine state of division, is dissolved in weak *aqua regia*, and to the dilute solution is added carbonate of soda to precipitate the metallic oxides; the liquid is then boiled with the precipitate for some time. After this the liquid is rendered acid with nitric acid, and digested at a gentle heat for several hours until the insoluble stannic acid has a perfectly white colour.

The stannic acid thus obtained is always perfectly free from copper; but it may still contain a trace of iron, so small however that in most cases it may be neglected. To get rid of it, it is requisite to redissolve the oxide of tin in hydrochloric acid, and to precipitate the tin by hydrosulphuric acid, &c. The oxide of tin, which is obtained by treating directly alloys of tin with nitric acid, is likewise ferruginous.

Separation of Nickel and Zinc.—The separation of these two metals, which occur together in several alloys used in the arts, is one of considerable difficulty. All the methods proposed for this purpose are either exceedingly tedious or very imperfect. The author states that their separation may be effected with accuracy by the following method, which is based on the fact that dilute hydrochloric acid has no action on the sulphuret of nickel prepared in the dry way, whilst it readily dissolves the sulphuret of zinc. The zinc and nickel are therefore precipitated simultaneously by carbonate of soda, the precipitate collected on a filter, dried and feebly calcined, then mixed with $1\frac{1}{2}$ time its weight of sulphur and $\frac{3}{4}$ths its weight of carbonate of soda, and this mixture heated for about half an hour in a small glass matrass at as high a temperature as the glass will bear. The substance is then treated with hydrochloric acid diluted with 10 times its weight of water several times, until it no longer dissolves any zinc, which is ascertained by testing the liquid after each treatment with carbonate of soda. The residue of sulphuret of nickel is then dissolved in *aqua regia*, and we have now only to precipitate the zinc and the nickel by carbonate of soda from their separate solutions.

When the alloy contains iron, if it has not been previously separated by ammonia from the nickel and zinc, it redissolves completely with the zinc on following the process just described.—*Bibliothèque Universelle*, April 1851.

On Schmidt's *Process for the Determination of Nitrogen.* *By* J. B. Bunce.

Chemists engaged in organic analysis have long felt the want of a quick and accurate process for the determination of nitrogen. Several objections may be offered to the method of Messrs. Will and

Varrentrapp, in following which the substance to be analysed is burned in contact with soda-lime; the ammonia formed is passed into a solution of hydrochloric acid gas, and after evaporation precipitated as ammonio-chloride of platinum. The more important of these arises from the solubility of the platinum salt, and the time required for the evaporation, drying, weighing, &c. In Liebig's Report for 1847 and 1848, mention is made of several new methods for the determination of nitrogen. Of these, that of Schmidt attracted my attention, and I was led to make some experiments upon it. He burns the substance as in the Will and Varrentrapp process, and passes the ammonia formed into a solution of 1 part chloride of barium in 8 parts of water; through this a constant stream of carbonic acid is passed, and from the precipitated carbonate of baryta the nitrogen in the analysed substance is calculated by equivalents. In experimenting on this process, I burned carefully-crystallized ferrocyanide of potassium, which had been proved pure by previous experiment; and I obtained results differing so widely from each other, that I was led to suspect some serious difficulty in the process. It was found upon trial that carbonate of baryta was partially decomposed by boiling with chloride of ammonium in a neutral solution, and also that chloride of ammonium when boiled by itself is converted into an acid salt. This holds true with many of the salts of ammonia with the stronger acids. A solution of chloride of calcium in alcohol produced no better results. The precipitated carbonate of lime was decomposed by the chloride of ammonium formed even in presence of alcohol.

I then tried some of the organic salts. Succinic acid gives with chloride of barium no precipitate; but upon the addition of ammonia, a fine crystalline precipitate is produced, only slightly soluble in water, and insoluble in alcohol. But as succinate of baryta is slightly soluble in ammoniacal salts, it was found that no use could be made of this method.

It would appear therefore that none of these modifications are capable of affording accurate results, and that the original process by Schmidt, unless some very essential feature is omitted in our account of it, must be considered faulty.—Silliman's *Journal*, May 1851.

On the Volatility of Phosphoric Acid in Acid Solutions.

By J. B. Bunce.

Rose, in a paper upon the determination of phosphoric acid, mentions the volatility of this acid with the vapour of water when evaporated in an acid solution. The object of the following experiments was to ascertain the extent of loss which would be suffered in analysis in consequence of this volatility. With this object in view, 0·544 grm. of phosphate of soda were dissolved in a gill of water; hydrochloric acid was then added, and the whole evaporated in a water-bath to dryness, being afterwards heated gently to drive off

any excess of acid. The residue was treated with strong sulphuric acid, and allowed to stand several hours in order to convert the pyrophosphate of soda into the ordinary tribasic salt. It was then diluted carefully, neutralized by ammonia, and precipitated as ammonio-phosphate of magnesia; the weight of this salt after ignition was 0·701 grm., equal to 0·045 of phosphoric acid. The consequent loss of phosphoric acid in this experiment was 58·66 per cent. Another experiment, in which the chlorine instead of the phosphoric acid was determined, gives as the loss of acid 53·36 per cent.

0·2 grm. of phosphate of magnesia and ammonia were next taken, dissolved in hydrochloric acid, diluted until about a gill of fluid was obtained, and the whole was then evaporated as before; after precipitation and ignition, the residue weighed 0·1316, corresponding to 41·69 per cent. of phosphoric acid. The per-centage of phosphoric acid in the ammonio-phosphate of magnesia, as determined by ignition, was 48·37 per cent. Consequent loss of phosphoric acid 6·67 per cent.

Another experiment, conducted in the same manner, with the exception that the pyrophosphate of magnesia was converted into the tribasic condition by fusion with carbonate of soda, gave 8·35 per cent. as the loss. The loss of phosphoric acid, when the solution was acidified with sulphuric acid instead of hydrochloric acid, was greater, probably owing to the higher degree of heat required to volatilize that acid. There was no perceptible difference between the action of hydrochloric and nitric acids. Phosphate of soda was completely converted into the sulphate of the same by three evaporations with sulphuric acid and water. Phosphates of alumina, iron, lime and magnesia were not perfectly converted into sulphates even by a dozen successive evaporations. Phosphoric acid does not seem to be more volatile in the vapour of alcohol than in that of water.

These experiments serve to show that the ordinary methods of analysis are not applicable to the analysis of phosphates which must be dissolved in acid by the aid of heat. In the ordinary evaporations to separate silica by rendering it insoluble, a very considerable loss of this acid is occasioned. The estimated quantity of phosphoric acid in ashes, &c. must probably in many cases be much too low, owing to this loss from volatilization; and we may believe that for this reason many analyses must be regarded as almost valueless with respect to the amount of phosphoric acid which they indicate.—Silliman's *Journal*, May 1851.

How to detect Oil of Turpentine in Petroleum.

According to M. Saladin, when petroleum containing oil of turpentine is triturated with iodide of potassium and water, it instantly acquires a yellow colour, and when the amount of oil of turpentine is large, an orange tint. One-thirtieth of oil of turpentine can be detected in this manner.—*Polytech. Blatt.*, No. xx.

PATENT.

Patent granted to Peter Claussen, *for certain Improvements in Bleaching, and in the Preparation of Materials for Spinning and Felting.*

This invention consists, first, in improvements in bleaching all kinds of vegetable productions, and fabrics or articles composed of such productions.

The ordinary process of bleaching fabrics, such as calico, consists in first immersing them in a bleaching liquor (commonly a solution of hypochlorite of lime, the chloride of lime of commerce), and then steeping them in a bath of water acidulated with sulphuric acid. By this means the chlorine is set free in its simple form, or in combination with oxygen (as chlorous or hypochlorous acid), or in chemical union with the hydrogen of the water (as hydrochloric acid); and thus it is either wasted by escaping, or else, by its remaining too long in contact with the fabrics, the latter are injured. Whereas, in bleaching according to this invention, the whole or a great part of the chlorine or "chloro-compound" is kept in a combined state, and recovered for future use. The patentee states, that, by the term "chloro-compound," he does not mean a salt containing chlorine, but an acid having chlorine for its base, such as chlorous or hypochlorous acid.

In bleaching according to this invention, the goods, after they have passed through the bleaching liquor (say a solution of hypochlorite of lime), are steeped in a strong solution of some salt whose acid has a greater affinity for lime than hypochlorous acid. Thus a strong solution of sulphate of magnesia may be used, the sulphuric acid of which, having a strong affinity for lime, combines with the earthy base of the bleaching salt, and forms sulphate of lime; and the chloro-compound, being thereby liberated, unites with the magnesia and forms hypochlorite of magnesia, which has bleaching properties similar to those of the hypochlorite of lime. This newly-formed compound may, in the next instance, be used as a primary bleaching agent, and be subjected to the process of double decomposition, as in the example just given. Thus the goods, after being subjected to the action of a solution of hypochlorite of magnesia, may be steeped in a liquid holding in solution some carbonate or other salt for whose base the hypochlorous acid has a greater affinity than for the magnesia; in which case the carbonic acid (if a carbonate be used), having a great affinity for the magnesia, combines therewith and forms carbonate of magnesia; and the liberated chloro-compound combines with the base of the carbonate employed to produce decomposition, and forms a new bleaching salt. This salt may also be employed as a primary bleaching agent, and be subjected to the process of double decomposition with similar results to those above stated. Thus if the carbonate used in the preceding example be carbonate of barytes, and a solution of sulphate of magnesia or of lime be brought into contact with the resulting chloro-

compound salt of barytes, sulphate of barytes will be precipitated, and the chloro-compound will unite with the magnesia or lime and form a bleaching salt.

In bleaching flax or other like vegetable material for making linen, no compounds should be used which are likely, during the decomposition of the same, to evolve any gaseous matters, such as carbonic acid or chlorine; as, by the development and expansion of the gas in the fibrous tubes, the flax or similar material would be rendered not so fit to be spun by the common flax spinning machinery; but in bleaching flax or similar material, which is to be combined with other materials for spinning and felting according to this invention, compounds evolving gas may be safely used, as hereafter explained.

The patentee does not confine himself to the use of the above-mentioned compounds for the purpose of bleaching by the method of double decomposition, nor to any particular salt or class of salts; but he claims a right to use any which, under the like circumstances, will be subject to the same chemical law of decomposition, and will produce the same result. He however points out, as among the salts suitable for decomposing the chloro-compound salts, or assisting in the process of bleaching, the carbonates (such as carbonate or bicarbonate of soda), sulphates (as sulphate of magnesia), nitrates (as nitrate of soda), acetates (as the acetates of potash and of lead), prussiates (as prussiate of potash), chromates (as chromate and bichromate of potash), and tartrates (as tartrate and bitartrate of potash).

Another method of bleaching, which is especially applicable to goods composed of both animal and vegetable fibres, consists in exposing the goods, after they have been steeped in any of the ordinary bleaching liquors (such as the solution of hypochlorite of lime), and while they are still wet, to the fumes of sulphur, produced by burning the same slowly in a suitable chamber or stove. In this case two powerful bleaching agents are brought into operation, viz. the hypochloritic compound and the sulphurous acid produced by the combustion of the sulphur. Part of the sulphurous acid combines with the base of the chloro-compound salt to form a sulphite of lime or magnesia, as the case may be; and a small portion of sulphuric acid may also be formed, which would form a sulphate of the base; by this means the chlorine or chloro-compound remaining in the wet goods is liberated, and permitted to exert its bleaching action upon the goods. The patentee states, that, in this process, certain chromates, manganates, hypermanganates, &c., may be occasionally substituted for the ordinary bleaching liquids.

The second part of this invention consists in improvements in the preparation of materials from flax, hemp, and other plants for spinning and felting.

The processes for preparing the materials, though possessed of some features common to the whole, vary according to the purposes to which the fibre is to be applied, that is to say, according as the fibre is required to be long or short, fine or coarse, and the machinery

by which it is to be spun is adapted for spinning one or other sort of fibre. The patentee states that by the term "fibre" he means that portion of each plant which is capable of being spun or felted; and the invention applies to the fibre surrounding the stems of *dicotyledonous* plants, and to that existing in the stems and leaves of *monocotyledonous* plants. In the following processes, flax or hemp is supposed to be the material under operation.

If the plant is to be operated upon from the time of its being cut down or pulled for use, it is taken in the state of straw (after the seed has been separated from it), and subjected to the following process:—The straw is steeped in a solution of caustic alkali of about 1° of Twaddle's hydrometer, for a suitable length of time; if dispatch is required, the solution is employed in a boiling state, which renders an immersion of about six hours sufficient; but if more time can be allowed, the solution may be used at a temperature of about 150° F., and the immersion prolonged for twelve hours; and the solution may even be used at a lower temperature with a corresponding prolongation of time; but in no case need the immersion exceed a couple of days. The objects of this process are,—first, to decompose, dissolve or remove the glutinous, gummy or other matters which connect the fibre with the woody portions of the plant; and secondly, to discharge or decompose any oleaginous, colouring or extraneous matter contained in the straw, without permitting such discharged matters to stain the fibre. The patentee generally uses a solution of caustic soda for effecting these objects; but other alkaline liquors (such as a solution of caustic potash or lime) will answer the purpose, as also will any substance having the like power of discharging, decomposing or removing the glutinous, gummy, colouring or other foreign matters contained in the straw.

If the fibre is required to be long, like that commonly spun in flax-spinning machinery, the straw is now treated in the following manner, to get rid of any of the alkali still adhering to the straw or fibre, and to complete the removal of any glutinous, gummy, colouring or other foreign matters:—The straw is taken from the alkaline solution above mentioned, and steeped for about two hours in water acidulated with sulphuric acid, in the proportion of 1 part of the acid to from 200 to 500 parts of water; some other dilute acids will answer this purpose, such as dilute muriatic acid, but sulphuric acid is preferred. Or the straw is transferred, while yet wet with the alkaline solution, to a suitable chamber or stove, wherein it is subjected to the action of sulphurous acid, or the fumes produced by the slow combustion of sulphur. In both cases the acid combines with any free alkali remaining on the straw or fibre, and forms a sulphite or sulphate thereof, according to the acid employed; while an excess of either sulphuric or sulphurous acid will complete the discharge, decomposition or removal of the glutinous, gummy, colouring and other matters. The straw is next removed from the acid bath or sulphur chamber, and washed or otherwise treated with water until all the soluble matters are removed.

If the fibre is required to be decolorized, the straw may now be

submitted to one of the above-mentioned bleaching processes, or to any of the ordinary bleaching processes; and after this it may be dried and made ready for breaking and skutching by the means commonly employed in the manufacture of long flax. In some cases it will be found advantageous to pass the straw between rollers, or to break it roughly or partially, before subjecting it to the above process, in order to facilitate the action of the chemical agents upon it. It is stated, that, by the above method, certain matters are removed from the straw which water alone cannot discharge; the fibre so prepared is also freer to heckle and the straw more easy to skutch than fibre and straw treated in the common way; much time and material are likewise saved, while the noxious exhalations attendant upon the water-retting system are entirely prevented.

If the fibre is required to be short, so that it may be felted or carded, and adapted for spinning on cotton, silk, wool, worsted or tow-spinning machinery, either alone or combined with cotton, wool, fur, hair, silk or "shoddy," the patentee takes the fibre, after it has been treated in the manner just described, and divides it into proper lengths by a suitable instrument or machine. The straw or fibre is then put into a bath containing a strong solution of bicarbonate, sesquicarbonate, or even carbonate of soda, or any similar compound (the first two being preferred, because they contain more carbonic acid); and it is permitted to remain in such bath for three or four hours, in order that the fibre may become well saturated with the salt. It is then immersed for about a couple of hours in water acidulated with sulphuric acid in the proportion of 1 part of acid to 200 parts of water; or else the saturated straw or fibre is exposed while wet to the action of burning sulphur in a suitable chamber or stove. In this operation it appears that a certain portion of gas becomes developed in the fibrous tubes, and by its expansive power it splits and divides them into filaments, having the character and appearance of fine cotton wool; and in this state they may be dyed and manufactured like cotton or wool.

As the same means of effecting the splitting of the fibre may be employed in the preparation of long fibre, the patentee does not confine himself to the use of the same for preparing short fibre alone; but he states, that, when the fibre is of its original length, the solution takes a longer time to penetrate into the interior. He likewise states, that the decomposition of the bicarbonate of soda, or other suitable compound, may be effected by electric agency, in which case a like evolution of gas and splitting up of the fibre will take place. After the fibre has been subjected to the splitting process, it must be carefully washed, to remove all soluble matters, and dried. The splitting process may be applied to the plant either in the straw (the wood of which is afterwards to be removed by suitable means), or in the state of long fibre, whether prepared by the above or any of the usual processes.—Sealed August 16, 1850.

THE CHEMICAL GAZETTE.

No. CCVIII.—June 16, 1851.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Compound Ammonias. *By* A. Wurtz.

[The author has published in a more complete form the results obtained in the further prosecution of his interesting discoveries. The following abstract, comprising the general results obtained in this investigation, will serve to complete the preliminary notices contained in former Numbers of this Journal*.—W. F.]

The so-called alcohol radicals, C^2H^3, C^4H^5, $C^{10}H^{11}$, can take the place of 1 equiv. hydrogen in another organic molecule, without the principal properties of the entire molecule experiencing any essential alteration in its chemical characters. In one of the simplest bodies of organic chemistry, ammonia, such a substitution occurs by methyle, C^2H^3, æthyle, C^4H^5, amyle, $C^{10}H^{11}$, new bases being produced which have the most perfect analogy with ammonia. These are methylamine, æthylamine and amylamine; the author first called them methylamide, &c., but gives the preference to the former denomination, as that agrees better with the general denomination used for the organic bases. They are all comprised under the collective name of compound ammonias.

The compound ammonias are produced, so far as is yet known, in four different ways:—

1. In the treatment of cyanic æther with potash, *Wurtz*.
2. In the treatment of cyanuric æther with potash, *Wurtz*.
3. In the treatment of urea with potash, *Wurtz*.
4. In the treatment of hydrobromic and hydriodic æthers with ammonia, *Hofmann*.

The reactions above indicated may be expressed in formulæ as follows:—

1. Mode of formation, *Wurtz*:—

$C^2NO, HO + 2KO + 2HO = 2CO^2, KO + NH^3$
Cyanic acid. Ammonia.

$C^2NO, C^2H^3O + 2KO + 2HO = 2CO^2, KO + C^2H^5N$
Methylocyanic æther. Methylamine.

$C^2NO, C^4H^5O + 2KO + 2HO = 2CO^2, KO + C^4H^7N$
Cyanic æther. Æthylamine.

$C^2NO, C^{10}H^{11}O + 2KO + 2HO = 2CO^2, KO + C^{10}H^{13}N$
Amylocyanic æther. Amylamine.

* Vol. vii. pp. 115, 141, 356, 377; vol. viii. p. 47.

2. Mode of formation, *Wurtz*.—The formation of the same terminal members from the cyanuric æthers is easily explained from the preceding. The above formulæ have only to be multiplied by 3, as the corresponding compounds of cyanuric acid are polymeric with the cyanic compounds.

3. Mode of formation, *Wurtz*:—

$C^2\ H^4\ N^2\ O^2 + 2KO + 2HO = 2CO^2, KO + NH^3 + NH^3$
Urea.

$C^4\ H^6\ N^2\ O^2 + 2KO + 2HO = 2CO^2, KO + NH^3 + C^2\ H^5\ N$
Methylic urea.

$C^6\ H^8\ N^2\ O^2 + 2KO + 2HO = 2CO^2, KO + NH^3 + C^4\ H^7\ N$
Æthylic urea.

$C^{12} H^{14} N^2 O^2 + 2KO + 2HO = 2CO^2, KO + NH^3 + C^{10} H^{13} N$
Amylic urea.

4. Mode of formation, *Hofmann*:—

$C^4\ H^5\ Br + NH^3 = HBr + C^4\ H^7\ N$
Bromide of æthyle. Æthylamine.

The compound ammonias are likewise formed under other circumstances, as for instance in the dry distillation of nitrogenous substances. Some years ago, Dr. Anderson isolated a very volatile base, petinine, from animal oil, and represented its composition by $C^8\ H^{10}\ N$. M. Gerhardt showed that it agreed better with the formula $C^8\ H^{11}\ N$, and was the butyric ammonia, or butylamine. Rochleder obtained methylamine from caffeine. Wertheim has described the formation of the compound ammonias in the distillation of morphine and narcotine with potash; by distilling the latter alkaloid with potash, he obtained the ammonia corresponding to metacetic or propionic acid, to which he gave the name of propylamine.

Methylamine, $C^2\ H^5\ N = 4$ vols. of vapour.—For the preparation of methylamine, the same method is followed as for ammonia. The muriate of methylamine is mixed with caustic lime in a long glass tube closed at one end, and in the upper part of the tube are placed fragments of caustic potash. The gas is expelled by a gentle heat, and is collected dry in a tube filled with mercury.

Properties.—A non-permanent gas, which condenses to a very mobile liquid a few degrees below 0° C., but which does not solidify in a mixture of æther and solid carbonic acid. It absorbs water from a moist atmosphere, and has a powerful ammoniacal odour; at 43° the density of the gas is 1·08; the theoretical density for 4 vols. is 1·0731. Of all the known gases, methylamine is that which is the most soluble in water. At 12°·5 C., 0·650 grm. water dissolved 750 cub. centims. gas; or 1 vol. of water dissolves, in round numbers, 1150 vols. of methyliac gas. At a higher temperature this solubility is smaller; at 25°, water only absorbs 959 times its volume. It is strongly alkaline, it instantly turns red litmus blue, diffuses dense white fumes when held near muriatic acid, absorbs an equal volume of muriatic gas, condensing with it into a salt perfectly similar to sal-ammoniac, but which subsequently deliquesces by absorption of

moisture from the air. With an equal volume of carbonic acid it gives solid carbonate of methylamine, which differs from carbonate of ammonia in being combustible. When set light to, it burns with a pale yellow flame into carbonic acid, water and nitrogen; when the combustion is imperfect, a little cyanogen or prussic acid is mixed with these products.

The analyses were made according to three different methods. The eudiometrical, by detonation with pure oxygen, gave, on combustion of 4 vols. methylamine gas with 9 vols. of oxygen, 4 vols. of carbonic acid, as follows:—

	I.	II.
Methyliac gas	23·3	26·5
Oxygen	67·7	71·0
Residue after combustion	49·0	51·8
Carbonic acid	23·2	26·0
Nitrogen	12·5	14·5
Oxygen absorbed	54·4	59·7

A very elegant and quick method of analysis consists in heating the gas with potassium; cyanide of potassium and pure hydrogen are formed, $C^2H^5N + K = C^2NK + H^5$. The following are some of the results obtained by this method:—

	I.	II.
Gas employed	37·5	31·5
Hydrogen	99·0	81·5

Thirdly, the author dissolved a certain quantity of the gas in water saturated with muriatic acid, and precipitated with bichloride of platinum; a double salt of methylamine and platinum was obtained, which on analysis led likewise to the above formula.

The aqueous Solution of Methylamine behaves exactly like a solution of ammonia towards other bodies. It precipitates salts of magnesia, manganese, iron, bismuth, chromium, uranium and tin. Zinc is at first precipitated, and then again dissolved by a large excess. Salts of copper are at first precipitated, but the precipitates subsequently redissolve with a blue colour in an excess. Salts of cadmium give a white precipitate; the precipitate does not redissolve in an excess, whilst it is dissolved by ammonia. Salts of nickel and cobalt behave like salts of cadmium towards a solution of methylamine. Acetate of lead is scarcely rendered turbid by methylamine; the nitrate is precipitated. Protosalts of mercury give a black precipitate; perchloride of mercury gives a white one, insoluble in an excess. Nitrate of silver furnishes a precipitate of oxide of silver, which dissolves completely in an excess. On evaporating the solution spontaneously, a black substance falls, which contains carbon, hydrogen, nitrogen and silver, and probably corresponds to the well-known explosive silver compound which is produced by ammonia; it, however, does not explode either by heat or percussion. Chloride of silver dissolves in a solution of methylamine. Perchloride of gold gives a yellowish-brown precipitate, which dissolves in an excess of the precipitant, forming an orange-red liquid. A concentrated

solution of bichloride of platinum furnishes with methylamine a substance crystallized in orange spangles, which however does not separate from dilute solutions.

Decompositions.—With potash it is evidently decomposed in two phases. At the commencement of the reaction, when the temperature is moderate, the volume of the gas increases but little, and the residue probably contains a compound analogous to the amiduret of potassium, $C^2(H^4K)N$. When the temperature is raised, this intermediate product, which I have not investigated, must be decomposed into hydrogen and cyanide of potassium; it is then that the volume of the gas increases considerably, and there is produced from 4 vols. = 1 atom of methylia, 5 atoms or 10 vols. of hydrogen, $C^2H^5N + K = C^2NK + H^5$. When passed through a tube filled with fragments of porcelain at a red heat, methyliac gas gives rise to the production of about 20 per cent. of prussic acid, being decomposed according to the equation—

$$3C^2H^5N = NH^3, C^2NH + C^2NH + C^2H^4 + H^6.$$

Action of Bromine and Chlorine.—Chlorine passed into an aqueous solution of methylamine yields, by partial decomposition, muriate of methylamine and oily drops, probably bichlorinated methylamine. Bromine acts in the same manner, hydrobromate of methylamine and a brominated methylamine soluble in water being produced.

Action of Iodine: *Biniodated Methylamine*, $C^2(H^3I^2)N$.—Iodine acts instantaneously upon methylamine, and forms a garnet-red powder. The liquid, when an excess of iodine has been avoided, is scarcely coloured, and contains hydriodate of methylamine in solution. The red insoluble substance is biniodated methylamine.

This is decomposed without explosion by heat, dissolves in alcohol, and leaves on evaporation a product of variable properties. Caustic potash decomposes it, iodide of potassium being formed, and a small quantity of a substance possessing a very powerful odour; and there is left as insoluble residue a few flakes of a yellow substance, which was not examined; it was however certainly not iodoform. Analysis furnished—

Carbon	4·12	..	2 =	12	4·27
Hydrogen	1·57	..	3	3	1·06
Iodine	90·35	88·70	2	252	89·32
Nitrogen	..	..	1	14	5·35

Hydrochlorate of Methylamine, C^2H^5N, ClH or C^2H^6N, Cl.—The gases produced in the decomposition of the methylocyanuric æther by potash are passed through a worm, when a portion of the water is condensed. The æther is very slowly decomposed by solution of caustic potash, but far more rapidly when fused with hydrate of potash and the addition of a very little water. The methyliac gas is collected in a receiver containing a little water, saturated with muriatic acid, and evaporated to dryness. The residue is dissolved in boiling absolute alcohol, from which the salt separates on cooling in large iridescent laminæ, which are deliquescent, and fuse above

100° C. When heated in open vessels, the salt rises in dense vapours, which condense upon cold bodies to a white powder. When the aqueous or alcoholic solution of the salt is treated with potassium amalgam, hydrogen is evolved, and the liquid becomes alkaline. An amalgam of methylammonium could not be prepared, even by submitting to the action of the battery a cupel formed of hydrochlorate of methylamine containing mercury. Analysis:—

Carbon	17·45	2 =	12·0	17·77
Hydrogen	8·78	6	6·0	8·88
Chlorine.....	52·45	1	35·5	52·52
Nitrogen	..	1	14·0	20·83

Double Hydrochlorate of Methylamine and Platinum, $C^2 H^5 N, Cl, PtCl^2$.—Beautiful yellow scales, soluble in hot water, crystallizing out on cooling, insoluble in alcohol. When heated, it turns black, giving off copious fumes, and leaves a residue of platinum mixed with carbon, which burns in the air. It furnished—

Carbon	5·3	5·0	5·3	2 =	12·0	5·0
Hydrogen	2·8	2·5	2·6	6	6·0	2·5
Chlorine.....	44·5	44·5	..	3	106·5	44·9
Platinum	41·44	41·0	41·7	1	98·6	41·9
Nitrogen	..	..	..	1	14·0	6·7

Hydrochlorate of Methylamine and Gold, $C^2 H^6 N, Cl, AuCl^3$.—A solution of perchloride of gold is mixed with a solution of muriate of methylamine; on evaporation, the salt crystallizes in magnificent golden needles, which are soluble in alcohol and æther:—

Carbon	3·03	2 =	12	3·21
Hydrogen	1·60	6	6	1·60
Chlorine.....	37·82	4	142	38·07
Gold	..	1	199	53·35
Nitrogen.....	..	1	14	3·77

Hydrochlorate of Methylamine and Mercury, $C^2 H^6 N, Cl, HgCl$, is obtained on evaporating a mixed solution of equivalents of hydrochlorate of methylamine and bichloride of mercury.

Hydrobromate of Methylamine, $C^2 H^5 N, HBr$ or $C^2 H^6 N, Br$, was obtained, as above stated, in the treatment of methylamine with bromine. It is soluble in water and alcohol, and crystallizes from the latter solution in large shining laminæ, which have a fatty appearance, and are not deliquescent. Analysis:—

Carbon	10·89	2 =	12·0	10·87
Hydrogen	5·65	6	6·0	5·43
Nitrogen	..	1	14·0	12·68
Bromine.....	..	1	78·4	71·02

Hydriodate of Methylamine, $C^2 H^6 N, I$.—Colourless laminæ, which turn brown in the air, are very deliquescent, and very soluble in water and alcohol.

Nitrate of Methylamine, $C^2 H^6 N^2 O^6$, is obtained by saturating an aqueous solution of methylamine with nitric acid; on evaporation,

it separates in right rhombic prisms resembling the nitrate of ammonia. They are deliquescent, and very soluble in water and alcohol. On distillation, they furnish gaseous products and oily drops insoluble in water. Analysis:—

Carbon	12·22	2 =	12	12·77
Hydrogen	6·44	6	6	6·38
Nitrogen	..	2	28	29·79
Oxygen	..	6	48	51·06

Sulphate of methylamine dissolves readily in water, but not in alcohol; it does not crystallize.

Methylic Urea, $C^2 \begin{matrix} H^3 \\ C^2 H^3 \end{matrix} N^2 O^2 = C^4 H^6 N^2 O^2$—When the solution of the above sulphate is evaporated with cyanate of potash and the residue exhausted with alcohol, this extracts an artificial urea, which forms a crystallizable salt with nitric acid, and which stands in the same relation to ordinary urea as methylamine to ammonia. The cyanate of methylamine experiences therefore at a moderate temperature the same alteration as the cyanate of ammonia.

Carbonate of Methylamine, $C^2 H^5 N, CO^2, HO$, may be obtained simply by distilling a mixture of carbonate of lime and muriate of methylamine. A concentrated solution of carbonate of methylamine collects in the receiver, in which a part separates in a solid and anhydrous form. On gently heating the whole, a portion of the solid salt is volatilized, whilst the remainder dissolves, and subsequently separates, when strongly cooled, in the hydrated state, in hard prismatic crystals. The following analyses show that these crystals were not pure, but a mixture of hydrated and anhydrous salts. The carbonate of methylamine is deliquescent, very volatile even at the ordinary temperature; its vapour is colourless and inflammable. Analysis:—

Carbon	30·8	32·1	3	= 18	33·96	3	= 18	29·03
Hydrogen	9·4	9·6	5	5	9·43	6	6	9·67
Oxygen	..	..	2	16	30·18	3	24	38·71
Nitrogen	..	..	1	14	26·43	1	14	22·59

Action of Methylamine on the Protochloride of Platinum.—The methylamine compound corresponding to Magnus's salt is formed when methylamine is added to protochloride of platinum suspended in water. The olive-coloured protochloride is then converted into a chrome-green powder, which contains 59·75 per cent. of platinum. The formula $2PtCl, 2C^2 H^5 N$ requires 59·72.

When this green compound is heated with nitric acid, red fumes are disengaged, and a gray powder, probably platinum, is eliminated. From the filtered liquid, after sufficient concentration, crystals separate, which undoubtedly constitute the compound analogous to Gros's salt.

The compounds analogous to the salts of Reiset are very readily obtained. The salt corresponding to Magnus's green salt is mixed in a flask with an excess of methylamine, and the flask then sealed before the blowpipe. When heated for some time on the water-bath, the

whole dissolves excepting a small quantity of a black powder; the flask is then opened, and the contents boiled to expel the excess of methylamine. The filtered colourless solution is evaporated to a syrup, and then set aside to crystallize; the crystals are separated and purified by recrystallization from water, and finally from alcohol. They furnished on analysis—

Carbon		12·28	12·36	4	=24·0	12·28
Hydrogen		5·00	5·22	10	10·0	5·09
Platinum	50·00	..	..	1	98·6	50·28
Chlorine..... ..		..	..	1	35·5	18·10
Nitrogen		..	..	2	28·0	14·25

leading to the formula—

$$C^4\,H\;PtN^2,HCl = \left.\begin{matrix} C^2\,H^5\,N \\ C^2\,H^4\,N \\ Pt \end{matrix}\right\} HCl.$$

Oxalate of Methylamine, $C^2\,H^5\,N, C^2\,HO^4$.—When oxalic acid is saturated with methylamine, a solution is obtained, which can be evaporated to a syrupy consistence, and crystallizes with great difficulty. The salt contained 59·6 per cent. of oxalic acid; the above formula requires 59·2.

Methylic Oxamide, $C^2\,\left.\begin{matrix} H \\ C^2\,H^3 \end{matrix}\right\} O^2\,N$.—The oxalate of methylamine yields, on dry distillation, methylic oxamide much more readily than oxalate of ammonia oxamide, from its being more volatile than the latter. It condenses in the neck of the retort in long slender needles. It is obtained still more readily by acting with methylamine upon oxalic æther.

It is more readily soluble in water than in alcohol. Alkalies resolve it into oxalic acid and methylamine. Anhydrous phosphoric acid carbonizes it. It gave on analysis—

Carbon	41·25	4	= 24	41·37
Hydrogen.....	6·99	4	4	6·89
Nitrogen	..	1	14	24·13
Oxygen.....	..	2	16	27·61

Binoxalate of Methylamine.—To the neutral salt a quantity of oxalic acid equal to that which it already contains is added. It crystallizes much more readily, and separates in small plates from the alcoholic solution.

Methyloxamic Acid, $C^4\,\left.\begin{matrix} H \\ C^2\,H^3 \end{matrix}\right\} NO^5$.—When the binoxalate of methylamine is exposed to a temperature of 160° C., it is decomposed into 2 equivs. water, which separate, and methyloxamic acid, corresponding to oxamic acid, the production of which is perfectly analogous. In this operation a part is found in the residue, another part in the neck of the retort in the form of a crystalline sublimate. But little acid is obtained; the greater portion is converted into neutral oxalate; the liberated oxalic acid into carbonic acid, carbonic oxide and water. The neutral oxalate formed then passes

into methylic oxamide, which is deposited in the neck of the retort in a crystalline state. The product is saturated with lime, when a mixture of the crystals of the lime salt and oxamide are obtained, from which the latter is expelled by heat, at which temperature the lime salt is not decomposed. When purified by recrystallization from water, this salt furnished on analysis—

Carbon	29·2	6 =	36	29·50
Hydrogen	..	4	4	3·27
Nitrogen	..	1	14	11·47
Oxygen	..	5	40	32·81
Lime	23·00	1	28	22·95

[To be continued.]

On the Corrosion of an Alloy, composed of Copper and Silver, in Sea-Water. *By* Aug. A. Hayes.

Some analyses I made many years since of sheathing copper, which had long resisted the action of sea-water, proved the presence of nearly one ten-thousandth part of silver. It was found that even this small portion of silver sensibly modified the chemical relations of the metal, and observations had indicated that the quality for sheathing was improved.

Copper of this kind is frequently met with in commerce, and is derived from the Chilian ores of copper, which, although argentiferous, do not yield enough silver to render its separation œconomical.

An occasion offered for again examining this subject when the argentiferous native copper of Lake Superior was first refined and rolled by the Revere Copper Company, more than five years since, and the results have lately been obtained.

Four suits of sheathing, for large merchant vessels, formed the subjects for observations, the metal being of uniform composition, as determined by assay of the clipping from many sheets. 2000 parts of the alloy contained 4 parts of pure silver, or the standard ton of this country contained 4 lbs. of silver.

A *proximate* analysis of this metal was also made, and it proved to be pure copper, throughout the mass of which an alloy of silver and copper was evenly distributed, so as to form either a mixture or a compound alloy, in which one part of the copper is truly combined with the silver, and the other larger part simply combines with the alloy. This is a very common constitution of alloys in which two metals exist, without any metalloid occurring to disturb the simplicity of the union, and always indicates a careful purification of the metals.

It was assumed as probable that the silver alloy would close the pores of the copper, which takes place with a tin alloy in bronze, and in a mechanical way confers durability. If however corrosion should take place, it must be in accordance with observed cases that the silver alloy would act as a negative element and the copper alone would be removed. How erroneous these inferences proved will be seen in the detail of the results.

The 'Chicora' was coppered Jan. 9, 1847, taking 7392 lbs. metal, which was fastened by bronze nails. She was employed in trade to China, and wore her copper so rapidly, that it was removed in March 1849, 2628 lbs. only remaining. In this case, the sheets, after the usual operations, had been consolidated by "cold rolling."

The 'Serampore' was coppered January 18, 1847, requiring 8447 lbs. of "cold rolled" metal, secured by bronze nails. She sailed to China and home *via* Cape of Good Hope, and to the Pacific and home *via* Cape Horn, requiring new copper in March 1850. The weight of the remaining copper was not ascertained.

The 'Hamilton' was coppered October 22, 1847, requiring 7706 lbs. metal, secured by bronze nails. The sheets used were in the ordinary or annealed state. This vessel was employed in the India trade, and wore out her copper in August 1849. The weight of the copper remaining was 3086 lbs.

The 'Carthage' was coppered November 26, 1847, requiring 8727 lbs. "cold rolled" metal, fastened by bronze nails. She was employed in the India trade, and her sheathing was destroyed in August 1849. The copper remaining weighed 5810 lbs.

Omitting the case of the 'Serampore,' where the corrosion cannot be determined by weight, we have the loss in every 100 parts of the metal for the time of duration; thus—

The Chicora, twenty-seven months, lost	64·45	per 100
The Hamilton, twenty-three months, lost	59·93	...
The Carthage, twenty-one months, lost	33·45	...

Allowing the same rate of corrosion, and taking the time as twenty-seven months for each—

The Chicora lost.....	64·45	in 100
The Hamilton lost	70·38	...
The Carthage lost	43·00	...

In the cases of the 'Hamilton' and 'Carthage' we perceive the influence of the different processes of manufacturing the sheets on the durability of the copper. By the operation of "cold rolling" the surfaces of the sheets are rendered very compact, and in any corroding solution they bear a negative relation to the metal in the same sheets between these surfaces. Such copper is also always strongly negative to annealed copper in acid solutions, until the hardened surfaces are removed; it then loses this relation. The 'Hamilton' exhibits the greatest effect of sea-water action on the annealed alloy, while in the 'Carthage' the protecting influence of the hardening surface was exerted nearly to the time her copper was removed.

These observations establish the fact of the rapid corrosion of an alloy thus constituted, and show its entire unfitness for sheathing purposes.

The average duration of copper sheathing decreases slightly, as the requirement of greater speed in sailing is more urgent. Taking one hundred merchant ships, sailing on different oceans, the average duration now on American ships is three years.

On the point of the *kind* of corrosion following the exposure of the alloy to sea-water and air, the information obtained in these trials is of a definite character. Part of the sheets remaining, and an ingot of the copper from smelting a large quantity, were assayed; and the results showed that the same proportion only of silver remained as was originally contained in the alloy. The silver alloy, therefore, by taking the negative state in the mass of the metal, hastened its destruction, while its own form and condition were such, that it separated as the copper was corroded.

For the records of facts, and much assistance continued for years in connection with the subject of copper corrosion, I am indebted to the kindness of my friend Mr. J. Davis, Jun., Treasurer of the Revere Copper Company.—Silliman's *Journal*, May 1851.

Researches on Cobalt. *By* E. Fremy.

I recently announced the existence of a series of ammonio-cobaltic salts, having as base ammonia or its elements combined with cobalt at different stages of oxidation*. My present object is to describe the mode of production of some new salts of cobalt, in which this metal is combined at the same time with oxygen and chlorine; the base of these salts is therefore a chlorinated oxide of cobalt.

When a current of chlorine is passed into an alkaline liquid holding protoxide of cobalt in suspension, the brown compound which is formed, and which is generally supposed to be sesquioxide of cobalt, frequently retains a considerable amount of chlorine, as I have ascertained by analysis.

Some salts of cobalt absorb chlorine directly, and produce chlorinated compounds. I found that acetate of cobalt rapidly dissolves chlorine, turns brown, and furnishes a salt in which the base is an oxide of cobalt corresponding to the sesquioxide, but in which a portion of the oxygen is replaced by chlorine.

It appeared to me interesting to examine whether chlorine might equally replace oxygen in those salts in which the bases were the ammonio-cobaltic oxides, and to determine whether the salts of cobalt, which when once dissolved in ammonia so readily absorb oxygen, might under the same influence unite with chlorine. But in these new experiments it was not possible to operate in the presence of ammonia, which is instantly decomposed by chlorine; it was requisite to act with hydrochloric acid upon the ready-formed ammonio-cobaltic salts. By the action of this acid I found that the ammonio-cobaltic base lost a portion of its oxygen, and united with an equivalent quantity of chlorine. In this manner I obtained a new series of salts, remarkable for their beautiful red-violet tint. When heated in a current of hydrogen, they furnish perfectly pure cobalt. As these new salts are almost insoluble in water, they are readily separated from the impurities which usually accompany cobalt, and may therefore be employed for the preparation of chemically-pure cobalt.

* Page 165 of the present volume.

The chlorine which exists in the chlorinated ammonio-cobaltic oxide is present in a peculiar state, for it is not precipitated immediately by nitrate of silver. This only happens after boiling, and we then reobtain the ammonio-cobaltic salts, in which oxygen has replaced the chlorine previously contained in them.—*Comptes Rendus*, May 26, 1851.

On the Composition of the Bitter Principle of Artemisia absinthium. *By* Dr. E. Luck.

Mein and Righini have described methods more or less tedious for preparing pure absinthine. The former chemist states that he obtained it crystalline and white*. To obtain this substance, I proceeded in the following manner:—The dry herb was exhausted with alcohol of 0·863, and the clear liquid distilled to the consistence of a syrup, the residue transferred into a stoppered bottle, and well shaken with æther. After some time this separates with a yellowish-brown colour. This treatment with æther is repeated until it no longer has a very bitter taste. The ætherial liquid is distilled in the water-bath; the residue consists of a viscid mixture of a blackish-brown acid resin and absinthine. On treating it with water to which a few drops of ammonia have been added, the black smeary resin is principally taken up, and the greater portion of the absinthine left behind.

In proportion as it becomes purer it acquires a pulverulent form. On adding a further quantity of ammonia, absinthine is also dissolved; but on triturating with concentrated ammonia, far less passes into solution, because the compound of ammonia with absinthine is very sparingly soluble in ammonia.

To remove the ammonia, it is now digested with dilute hydrochloric acid, then washed with water, dissolved in alcohol, and solution of acetate of lead mixed with it as long as any turbidity results, filtered, and sulphuretted hydrogen passed into the liquid in order to decompose the excess of the lead salt. The alcoholic solution filtered from the sulphuret of lead is mixed with a small quantity of water, allowed to evaporate slowly in a warm place, when the absinthine separates in yellow resinous drops. These are soft, become coated when mixed with water with an opake membrane, and in the course of some weeks all the drops become converted into hard masses, which externally are jagged and rough, internally, radiate and indistinctly crystalline.

The colour is brownish-yellow to yellow; when pulverized, it furnishes a yellowish powder, of a faint, disagreeable, bitter odour of wormwood; it has an intensely bitter taste, is sparingly soluble in water, and melts in boiling water. It dissolves readily in alcohol, somewhat less in æther, and is likewise soluble in concentrated acetic acid, from which it is partially precipitated by water. It has a tolerably acid reaction, and dissolves, as above stated, somewhat in an aqueous solution of ammonia, but far more readily in caustic potash, with a golden-yellow colour. Cold sulphuric acid dissolves

* See Dr. Zwenger's observations on this subject in Chem. Gaz., vol. ii. p. 124.

it at first with a reddish-yellow colour, which however quickly turns indigo-blue by exposure to the air, apparently with absorption of oxygen. Water produces in this blue solution a dirty gray-green flocculent precipitate, and the supernatant liquid is of a rose colour. After the flakes have been washed on the filter with water, they dissolve readily in alcohol with a yellow colour, but sparingly in æther. This substance has no longer a bitter taste; and its spirituous solution leaves on evaporation a violet-blue amorphous residue, which again dissolves with a yellow colour.

Hydrochloric acid dissolves absinthine with a yellow colour, which on the application of a gentle heat passes into red; subsequently the colour becomes darker, with a turbidity and separation of a brown mass: it dissolves in fuming sulphuric acid with a brown colour. Heated upon platinum foil, it is partially volatilized in brownish-yellow bitter vapours, which condense into an amorphous substance, but the greater portion is carbonized. The substance, dried *in vacuo* over sulphuric acid, gave the following analytical results:—

Carbon	65·06	65·30	16 =	96	65·30
Hydrogen	7·60	7·65	11	11	7·48
Oxygen	..	..	5	40	27·22

The empirical formula for absinthine is therefore $C^{16} H^{11} O^5$, the rational formula probably $C^{16} H^{10} O^4 + HO$. The preparation of a pure compound of absinthine with a metallic oxide of constant composition is exceedingly difficult.

Absinthine was dissolved in alcohol and mixed with some caustic potash, carbonic acid passed into the dark golden liquid as long as carbonate of potash separated, and then some æther added and filtered. In this solution of absinthine and potash acetate of lead produced a beautiful yellow flocculent precipitate of absinthine and oxide of lead; but in the course of a few minutes it was converted into heavy white oxide of lead, and the alcohol became coloured yellow by dissolved absinthine. It was also found impossible to obtain the potash compound in a solid form. The spirituous solution of the bitter principle gives no precipitate with neutral acetate of lead, and but a slight turbidity with basic acetate of lead; I succeeded however in obtaining a lead compound in the following manner:—Basic acetate of lead and some ammonia were added to an alcoholic solution, and evaporated to dryness *in vacuo* over sulphuric acid. The dry residue was rubbed to powder, and treated first with water, and after drying with æther as long as anything was dissolved, and lastly alcohol was employed for washing. This compound gave 55·25 per cent. oxide of lead, leading to the formula $2(C^{16} H^{10}) O^4 + 3PbO$, which requires 54·80 oxide of lead.—Liebig's *Annalen*, April 1851.

Antiseptic Properties of Chloroform.

According to M. Augendre, $\frac{1}{2\,0\,0}$th part of chloroform suffices to preserve 1 part of flesh from putrefaction.—*Comptes Rendus*, xxxi. p. 679.

Contributions to our Knowledge of the Isomeric Acids.
By Prof. J. GOTTLIEB.

Citraconic and Itaconic Acids.—The author first shows, by the analysis of a silver salt, that citraconic acid is bibasic, as has generally been admitted of late. When the acid is saturated with ammonia, and nitrate of silver added to the neutral solution, the neutral salt described by Crasso separates in crystalline flakes. The author dissolved this in hot water, and obtained by successive crystallizations, at first the neutral salt in larger crystals, but finally an acid salt, the production of which is easily explained from the circumstance that ammonia escapes during the evaporation of the solution of the ammonia salt. The salt is obtained more easily by dissolving the neutral salt in aqueous citraconic acid, and allowing the solution to evaporate spontaneously. The acid salt then separates in pretty large anhydrous crystals, which are much more soluble in water than the neutral salt. Their analysis led to the formula $C^{10} H^5 O^7, AgO$, as follows:—

Carbon	25·10	10 =	60	25·31
Hydrogen	2·42	5	5	2·12
Oxygen	26·83	8	64	27·00
Silver	45·65	1	108	45·57

Experiments made in the same manner with itaconic acid showed that this acid is monobasic; no acid salt could be produced.

Mesaconic Acid, $C^5 H^3 O^4$, a new acid isomeric with the two preceding ones. When citraconic is treated with nitric acid, the products are different according to the concentration of the acid. Nitric acid of 1·47 spec. grav. mixed with a saturated solution of citraconic acid exerts a very lively and sometimes very violent action. When a dilute solution of citraconic acid is mixed with the sixth part of nitromuriatic acid and heated to boiling, a quiet disengagement of gas ensues; and on cooling, porcellaneous masses of the new acid separate.

Mesaconic acid has an astringent taste, is very sparingly soluble in cold and readily soluble in hot water; it has a great tendency to effloresce from the aqueous solution. It dissolves in alcohol. At 406° F. it melts to a clear fluid, and may be sublimed unaltered a few degrees higher. The fused acid congeals on cooling to a crystalline mass. Its vapour is pungent and excites coughing; its solution strongly reddens blue litmus-paper and decomposes the carbonates. The hydrated acid, dried at 212°, furnished on analysis—

Carbon	45·73	45·77	5 =	30	46·15
Hydrogen	4·61	4·57	3	3	4·61
Oxygen	49·66	49·66	4	32	49·24

Mesaconate of Silver, $C^5 H^3 O^3, AgO$, obtained by precipitating a solution of the acid neutralized by ammonia with nitrate of silver. It is a heavy white crystalline precipitate, which is not altered by light nor by being heated to 212°, and exhibits the property observed in itaconate of silver, of extending itself in a vermicular form

on the application of heat. The salt, dried at 212°, furnished on analysis—

Carbon	17·72	5 =	30	17·44
Hydrogen	1·24	2	2	1·17
Oxygen	18·55	4	32	18·60
Silver	62·49	1	108	62·79

Citraconimide, $C^{10}H^5O^4N$.—In accordance with our present knowledge of the organic acids, and especially of those whose deportment towards ammonia and aniline has been more accurately examined, that the bibasic acids (as succinic, phtalic, camphoric, &c.) form imides and anilcs, whilst the monobasic acids do not furnish these compounds, we find that the bibasic citraconic and mesaconic acids yield an imide and an anile, whilst itaconic acid gives no such compound. Citraconic acid, mixed with an excess of ammonia and evaporated to dryness in the water-bath, yields a mixture of neutral and acid ammonia salt; the pure acid salt is not so well adapted for the production of the imide as this mixture. When this is gradually heated in a retort, a large amount of ammoniacal water is at first given off. As soon as the temperature approaches 356°, the yellowish liquid puffs up considerably, the production of water ceases, and the whole solidifies to a vitreous amber-coloured mass, which cannot be heated further without being entirely decomposed, becoming black and fusing. This mass is citraconimide. It has a conchoidal fracture, is insoluble in cold, soluble in boiling water, when the excess of substance melts to a tenacious liquid, while the dissolved portion separates on cooling in small drops, which subsequently solidify. Citraconimide dissolves somewhat in alcohol with the same phænomena. It is tenacious, and is difficult to pulverize. The fine powder is perfectly white. In this state it is very hygroscopic, and can no longer be freed from adherent water at 212°. It is inodorous. The analysis of the substance, dried at 356°, at which temperature it parts with its water, furnished—

Carbon	54·18	10 =	60	54·05
Hydrogen	4·66	5	5	4·51
Oxygen	28·57	4	32	28·83
Nitrogen	12·59	1	14	12·61

Citraconimide boiled with ammonia dissolves in it, and does not separate on cooling; undoubtedly *citraconaminic acid* is formed. The baryta salt of this acid is soluble in water, and is precipitated from it by alcohol in yellowish flakes. It melts readily at a gentle heat so long as it is moist. The dry salt does not melt at 212°. The moist lead and silver salts are of the consistence of a plaster, and melt when warm, but not the dry salts; all three salts are yellow. The author could not procure any imide from itaconate of ammonia.

Citraconanile, $C^{22}H^9NO^4$, is readily formed on mixing anhydrous citraconic acid with aniline and gently heating; further, when an aqueous solution of citraconic acid is mixed with aniline as long as any is dissolved, and then heating to ebullition or evaporating

on the water-bath. No aniline salt of citraconic acid appears to be produced in this operation, or else it is only capable of existing in the cold solution; thus when the bicitraconate of ammonia, dissolved in water, is mixed with aniline and boiled, the whole of the aniline is converted into citraconanile with disengagement of ammonia. This compound is also formed when anhydrous citraconic acid is heated with a large excess of aniline in a retort; the excess of aniline distils off, and the residue is citraconanile. Two other modes of production will be subsequently mentioned. When the citraconanile has been purified by recrystallization, it forms brittle crystals, which are easily reduced to powder, and melt at 205° to a yellowish liquid; when this takes place in boiling water, the drops sink to the bottom. Heated above 212°, citraconanile evaporates readily, and can be sublimed unaltered in small quantities, when it is deposited in colourless needles on the sides of the vessel. When the evaporation is carried on slowly, it diffuses a faint odour of roses; but large quantities of the vapour have a pungent odour, and excite coughing. The boiling neutral liquid soon becomes acid, and then contains citraconic acid. Citraconanile is easily soluble in alcohol and æther, and separates on evaporation in shorter and more distinct crystals than from the aqueous solution. Their form however could not be determined. Solutions of the anile are not altered by chloride of lime. A deal shaving is coloured brownish-yellow by aniline in the boiling aqueous solution.

Citraconanile cannot be combined with acids or with bases, but it dissolves abundantly at the ordinary temperature in the hydrate of sulphuric acid, colouring this reddish-brown. Water causes a separation of unaltered citraconanile. Analysis of the compound, dried *in vacuo* over sulphuric acid, gave—

Carbon.....	70·36	70·54	..	22	132	70·58
Hydrogen....	4·89	4·93	..	9	9	4·82
Nitrogen	..	..	7·69	1	14	7·48
Oxygen.....	..	..	..	4	32	17·12

Citraconanilic Acid, $C^{22}H^{11}NO^6$, is formed from citraconanile when this is boiled for a short time with dilute ammonia. On the addition of acetic acid, the citraconanilic acid forms a heavy white crystalline precipitate, which is washed with cold water, and separated as much as possible between paper from adherent mother-liquor. The undecomposed citraconanile crystallizes from the mother-liquor after some time in long colourless needles. The acid is recrystallized from a mixture of equal parts of alcohol of 0·863 and æther, when, on cooling and evaporation, pure acid crystallizes at first, and subsequently mixed with citraconanile.

Pure citraconanilic acid forms small, heavy, shining crystals, which have a distinctly acid reaction. When heated to fusion, they part with water, and are converted into citraconanile. At 212° the hydrate is unaltered. The acid is very unstable; the hydrate is not soluble in water; when boiled with it, the acid disappears, being decomposed, and does not again separate on cooling. When the

pure hydrate is neutralized with ammonia, and the solution mixed with nitrate of silver, a white precipitate falls, which turns black, especially on ebullition with water. The beautifully red-coloured solution produced by the partial decomposition deposits on cooling crystals of citraconate of silver. The pure hydrate, mixed with water and carbonate of baryta, and warmed, furnishes citraconate of baryta, with disengagement of carbonic acid. The analysis of the hydrated acid, dried at 212°, furnished—

Carbon	64·40	22 =	132	64·39
Hydrogen	5·54	11	11	5·36
Nitrogen	..	1	14	6·83
Oxygen	..	6	48	23·42

Itaconanilide, $C^{17} H^{8} NO^{2}$, is formed when the hydrate of itaconic acid is heated with an excess of aniline in a retort to 360°. The excess of aniline distils off; the residual brownish liquid solidifies on cooling to a crystalline mass, and is impure itaconanilide, which is dissolved in alcohol of 0·863 spec. grav., and obtained perfectly pure by recrystallization. The dry substance is very loose, has a faint lustre, is adhesive and soft; it easily cakes together. Pressed while moist between paper, it forms a connected mass with a lustre of mother-of-pearl. It dissolves easily in æther, scarcely at all in cold, and but sparingly in hot water, separating on cooling in minute spangles. It melts at 365° into a slightly-coloured liquid, and solidifies on cooling into dull crystalline masses. It can be sublimed unaltered in small quantities; its vapour has a pungent odour. Dilute aqueous alkalies have no perceptible action upon itaconanilide either at the ordinary temperature or on ebullition, nor is it altered by dilute acids. Sulphuric acid ($SO^{3} HO$) dissolves it with the same phænomena as citraconanile. Dried at 212°, it furnished—

Carbon	72·45	73·15	72·91	17 =	102	72·85
Hydrogen	5·94	5·83	5·76	8	8	5·72
Nitrogen	..	..	..	1	14	10·00
Oxygen	..	..	..	2	16	11·43

Itaconanilic Acid, $C^{22} H^{11} NO^{6}$.—When itaconanilide is fused with itaconic acid, no itaconanilic acid is formed; but it is readily produced when an excess of itaconic acid is mixed with aniline, the solution of the acid itaconate evaporated to dryness, and then heated somewhat above 212°. This acid is more stable than citraconanilic acid, and may be recrystallized from hot water, from which it separates in broad, colourless, shining needles. From alcohol, in which it is more readily soluble than in water, it is obtained in aggregations of tabular crystals. The aqueous solutions of its salts deposit it upon the addition of an acid in the form of a white crystalline precipitate. Neither the hydrate nor the salts are coloured by chloride of lime. At 372° it melts and undergoes partial decomposition. The crystals of itaconanilic acid are brittle and easily reduced to powder; dried at 212°, they furnished—

Carbon	64·35	22 =	132	64·39
Hydrogen.....	5·33	11	11	5·36
Nitrogen	..	1	14	6·83
Oxygen.....	..	6	48	23·42

Itaconanilate of Silver, $C^{22}H^{10}NO^5$, AgO (dried at 212°).—This silver salt forms a crystalline precipitate, which dissolves in hot water with partial decomposition, and separates in broad shining spiculæ. It gave on analysis—

Carbon	42·47	22 =	132	42·31
Hydrogen.....	3·37	10	10	3·21
Nitrogen	..	1	14	4·48
Oxygen	..	6	48	15·39
Silver	34·80	1	108	34·61

Itaconanilate of Baryta, $C^{22}H^{10}NO^5$, BaO, is formed on boiling itaconanilic acid with water and carbonate of baryta. It is a very soluble salt, does not crystallize, but remains gummy, puffs up considerably at 338° without decomposition, and contains at this temperature 28·07 baryta.

Itaconanilate of Soda is obtained by saturating the acid with soda. It crystallizes imperfectly from syrupy solutions.

Itaconanilate of Copper, $C^{22}H^{10}NO^5$, CuO, is formed by precipitating sulphate of copper with the soda salt. It is a pale blue crystalline precipitate, and furnished 16·84 per cent. oxide of copper, which is the quantity required by theory.

Itaconanilate of Lead is a white caseous precipitate, very similar to the chloride of lead; and when kept long in the liquid, is converted into beautiful tufts of crystals.

When itaconanilic acid is saturated with ammonia and the solution evaporated, a sparingly-soluble residue of an acid ammonia salt is left, which can be obtained in groups of minute crystals from hot water.

When heated to 374°, the acid fuses without any perceptible change; but at 500° it parts with water, and a great portion of the acid is converted into citraconanile, citraconic acid, itaconanilide and itaconic acid, of which the two first distil over, whilst the two latter remain mixed with the still-undecomposed itaconanilic acid. The property of the hydrate of itaconic acid, of furnishing citraconic acid upon distillation, is therefore repeated in its anilides. The acid parts with 2 equivs. water, but at the same time passes into the citraconic group: $2(C^5H^2O^2)$ give $C^{10}H^4O^4$, and with the remainder of the aniline $C^{12}H^5N$, citraconanile. Another portion is resolved into the anilide and itaconic acid, $C^{22}H^{11}NO^6 = C^{17}H^8NO^2 + C^5H^3O^4$; but the latter at the temperature at which it is produced is converted partly into water and anhydrous citraconic acid, which are volatilized with the citraconanile. The distillate was treated with boiling water, from which on cooling the citraconanile separated.

The brownish residue which crystallized on cooling was dissolved in hot alcohol, and poured into cold water. A mixture of itacona-

nilide and anilic acid separated in crystalline flakes. The filtered liquid gave on evaporation a few crystals of itaconic acid. The substance precipitated by water was dissolved in alcohol, and mixed with water containing ammonia, which held the itaconanilic acid in solution. The precipitate now obtained recrystallized from alcohol was pure itaconanilide.

Mesaconanilide.—The author has not yet succeeded in obtaining this compound. The acid is decomposed under the conditions requisite for the preparation of this body into citraconic acid, and then furnishes citraconanile. The concentrated aqueous solution of mesaconic acid, mixed with aniline as long as any is dissolved, gives no sparingly-soluble substance on ebullition; even after long application of heat the liquid contains undecomposed aniline, and is coloured by chloride of lime. On evaporation, crystalline masses of the aniline salt separate; when this, after being dried, is conveyed into a retort, and heated to 464°, it melts, and a mixture of aniline, citraconanile and water distil over. When the greater portion of the substance so modified has passed over, an inconsiderable tenacious brown residue is left in the retort. Water always makes its appearance simultaneously with aniline and citraconanile; consequently the decomposition of the aniline salt takes place concurrently with the formation of citraconanile. When the heating was interrupted before the decomposition was complete, the residue contained citraconanile along with mesaconate of aniline.

Citraconiodanile, $C^{22}H^{8}INO^{4}$.—Iodide of aniline, which had been prepared according to Hofmann's direction, gave, on being boiled with water and excess of citraconic acid, with precisely the same appearances as have been described in the analogous formation of citraconanile, a sparingly-soluble product in water, which, after being purified by two recrystallizations from hot water, gave pure citraconiodanile. This separates from the hot aqueous solution in slender needles, which have the greatest resemblance to citraconanile, only that they are considerably smaller and slightly yellowish. It is readily soluble in alcohol. When fused, it is decomposed with disengagement of vapours of iodine, whilst a portion appears to sublime unaltered. Dried at 212°, it furnished on analysis—

Carbon	42·04	22	132·00	42·16
Hydrogen.....	2·82	8	8·00	2·55
Iodine	..	1	127·08	40·59
Nitrogen	..	1	14·00	4·47
Oxygen	..	4	32·00	10·23

The author adopts the rational formula for citraconiodanile to accord with Hofmann's view, according to which aniline is ammonia in which one H is replaced by phenyle, viz.

$$\left.\begin{matrix} C^{5} & H^{2} & O^{2} \\ C^{5} & H^{2} & O^{2} \\ C^{12} & (H^{4} & I) \end{matrix}\right\} N.$$

Liebig's *Annalen*, lxxvii. p. 265.

Mode of distinguishing artificial from natural Camphor. By J. W. Bailey.

By the application of polarized light, the smallest portion of natural camphor may be distinguished from the artificial camphor (hydrochlorate of camphene). If small fragments of each be placed separately on glass slides, and a drop of alcohol added to each, they dissolve and speedily recrystallize. If the crystallization of the natural camphor is watched by means of the microscope and polarized light, a most beautiful display of *coloured* crystals is seen, while with the artificial product nothing of the kind is witnessed. —Silliman's *Journal*, May 1851.

PROCEEDINGS OF SOCIETIES.

Royal Society.

April 10, 1851.

"On the Molecular Constitution of the Organic Bases." By Dr. Hofmann.

In a former paper* the author advanced a general theory regarding the constitution of the *volatile* organic bases. He showed that in all these substances the original structure of ammonia may be traced without difficulty, and that they must be viewed as ammonia in which either one, two, or the three equivalents of hydrogen are replaced by a corresponding number of compound molecules; he accordingly distinguished the volatile bases as amidogen, imidogen, and nitrile bases.

Ammonia. Amidogen bases. Imidogen bases. Nitrile bases.

In his present memoir he goes a step further, and communicates the discovery of a new group of alkaloids, closely connected by their origin and composition with the former class, but differing from it altogether by their properties. These new alkaloids are no longer *volatile* without decomposition, and form in this manner the connecting link between the artificial bases, nearly all of which are volatile, and the natural alkaloids, the majority of which are of a fixed nature.

The alkaloids of the new class, to which for the sake of convenience the author assigns the term of ammonium bases, arise from the nitrile bases by the assimilation of the additional equivalent of one of the replacing molecules in conjunction with oxygen and water.

* Chem. Gaz., vol. viii. p. 276.

$$\left.\begin{matrix} V \\ X \\ Y \end{matrix}\right\} N + ZO,\ HO = \left.\begin{matrix} V \\ X \\ Y \\ Z \end{matrix}\right\} NO,\ HO.$$

In his memoir the author establishes the conditions under which this transformation takes place, viz. the action of the alcohol iodides on nitrile bases, and he developes the generality of his observations by the description of about a dozen of new alkaloids prepared according to his method; he points out moreover that the number which may be actually produced is nearly unlimited.

The new substances which are formed under the above conditions, are endowed with very remarkable properties. The alkaloid which is formed by the union of four ethyl equivalents with nitrogen, oxygen and water, the substance in which $V=X=Y=Z=C_4H_5$, *i. e.*

$$\left.\begin{matrix} C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \\ C_4\,H_5 \end{matrix}\right\} NO,\ HO,$$

is thus described by the author.

It is of a powerfully alkaline reaction, which manifests itself, not only in its deportment with vegetable colours, but also in its combining their pungent taste with the bitterness of quinine. The solution, when concentrated, not only burns the tongue, but it acts strongly upon the epidermis, which it destroys, like caustic potassa or soda; on rubbing a solution of the oxide between the fingers, we feel the well-known sensation produced by the fixed alkalies under the same circumstances, and we perceive moreover the same peculiar odour. Oxide of tetræthylammonium, as the author calls this substance, saponifies the fats as readily as potassa. The experiment was made with cocoa-nut oil, which, after half an hour's ebullition with the new alkali, was converted into a beautiful soft soap, having the appearance of an ordinary potassa soap.

The author has traced the analogy of the new compound with potassa in many other directions, and especially in its deportment with the metallic oxides: his alkaloid, in fact, produces with the salts of the metals exactly the same reactions as potassa.

The other substances belonging to this group have similar properties, modified only by the character of the replacing molecules. Among them are several which are remarkable for the complex nature of their constitution, which, nevertheless, is perfectly intelligible.

In conclusion, the author draws attention to the assistance which the solution of the grand problem of preparing artificially the natural alkaloids, especially those of the cinchona bark, may receive from a further extension of these researches. He shows that even now the analogy in the general deportment of his ammonium bases, and the alkaloids of nature, is very great, although they differ materially in many properties.

THE CHEMICAL GAZETTE.

No. CCIX.—July 1, 1851.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Colouring Matters of Fustic (Morus tinctoria).

By Dr. R. WAGNER.

THE first part of this investigation (pp. 1, 21) contained a description of the method of preparing pure moritannic acid and morine, their properties and constitution, deduced from analyses. The present part treats of the products of decomposition, which were only briefly alluded to in the former paper.

Action of Heat upon Moritannic Acid.—When moritannic acid is exposed in a retort to a gentle heat, it melts, and is decomposed into carbonic acid, a colourless oily liquid, which distils over, and a residual bulky cinder. The colourless liquid soon concretes to a crystalline mass, which smells of phenylous (carbolic) acid, and can be freed by pressure between blotting-paper from an uncrystallizable oil.

To prepare the crystalline product in large quantity, crude moritannic acid was mixed with an equal bulk of quartz sand, and the mixture exposed to a very gentle heat in a retort. The yellowish-white crystals obtained on the solidification of the liquid which had passed over were purified by sublimation; they then formed a perfectly white, crystalline, tolerably hard mass. The author calls this substance

Pyromoritannic Acid, $C^{12}H^6O^4$.—It dissolves easily in water, more readily in alcohol, but sparingly in æther. From the aqueous solution it separates in shining crystals, which are small rectangular prisms. The acid recrystallized from water has scarcely a perceptibly acid reaction; its taste is somewhat bitter, and resembles phenylous acid. The aqueous solution reduces perchloride of gold, nitrate of silver and bichloride of platinum with great ease; produces no change in protosalts of iron; but strikes, with the perchloride of iron, or with the ferroferric oxide, a dark green colour, which passes into a dark red upon the addition of ammonia, potash or barytic water. The solution of the acid in potash or ammonia absorbs oxygen from the atmosphere, and turns green, then brown, and after a short time becomes opake and black; solutions of the carbonated alkalies exhibit a similar behaviour towards this acid. When a drop of the concentrated aqueous solution is added to milk of lime, no purple-red colour is produced, as is the case with pyrogallic acid, but the liquid assumes a lively green colour, which passes into brown. When a deal shaving is dipped into a solution

of the pyroacid, then drawn through dilute hydrochloric acid, and afterwards exposed to sunlight, the wood acquires a faint violet colour, but the purer the acid the fainter is the colour; so that a perfectly pure acid, free from every trace of the oily collateral product above mentioned, does not give the reaction with a deal shaving. Pyromoritannic acid gives no precipitate with solution of gelatine, tartrate of antimony and potash, or with salts of quinine. The crystals, dried at 176° F., melt at 212°; the fused mass begins at 266° gradually to evaporate, and between 464° and 473° boils violently. The vapours are colourless, and condense into a liquid, which coats the neck of the retort with crystalline arborizations. With neutral acetate of lead the solution of the pyroacid furnishes a white precipitate, which is insoluble in water, and consists of a combination of the pyroacid with oxide of lead. A solution of sulphate or acetate of copper, to which potash has been added, is reduced by pyromoritannic acid on ebullition. The substance, dried at 176°, furnished—

Carbon	65·51	12	= 72	65·45
Hydrogen	5·86	6	6	5·46
Oxygen	..	4	32	29·09

In order to prepare the lead salt for the purpose of determining the atomic weight of the acid, an aqueous solution was precipitated with neutral acetate of lead, the white precipitate well washed and pressed between blotting-paper. When dry, it formed a greenish-white powder; two determinations of the oxide of lead furnished 69·5 and 68·1 per cent. oxide of lead.

The lead salt has most probably the following constitution:—

$$C^{12}H^4O^2, 2PbO = C^{12}\left\{\begin{matrix}Pb^2\\H^4\end{matrix}\right\}O^4.$$

This formula requires 70·7 per cent. oxide of lead, which differs somewhat from the preceding determinations, but is highly probable from the great unstableness of the lead salt.

The new acid differs from pyrogallic acid, $C^{12}H^6O^6$, by containing 2 atoms of oxygen less, and by its deportment towards peroxide of iron and milk of lime; in other respects it has the greatest resemblance to it. In the same manner as pyrogallic acid is produced from quercitannic acid, pyromoritannic acid is formed from moritannic acid, for—

$C^{18}H^8O^{12}$, quercitannic acid.	$C^{18}H^8O^{10}$, moritannic acid.
$-C^{12}H^6O^6$, pyrogallic acid.	$-C^{12}H^6O^4$, pyromoritannic acid.
$C^6H^2O^6$	$C^6H^2O^6$

Pyromoritannic acid is polymeric with the colourless hydroquinone of Wöhler, and stands, as regards its formula, in close relation with japonic acid, $C^{12}H^4O^4$, and the isomeric quinone, with rubinic acid, $C^{12}H^4O^6$, and the isomeric quinonic acid (melanic acid).

It is further homologous with saligenine—

$$C^{14}H^8O^4 = C^{12}\left\{\begin{matrix}H^5\\C^2H^3\end{matrix}\right\}O^4,$$

with which it has several properties in common. From orcine, which is isomeric with saligenine, the formula of pyromoritannic acid likewise differs only by $-C^2H^2$, and from β orcine, $C^{16}H^4O^4$, by $-2C^2H^2$. Which of the two compounds, saligenine or orcine, is homologous with pyromoritannic acid will be shown by the products of decomposition. If saligenine is the homologous body, pyromoritannic acid should be converted by oxidizing agents (as chromic acid and oxide of silver) into a substance, $C^{12}H^4O^4$, which would be analogous and homologous with hydruret of salicyle—

$$C^{12}H^6O^4+2O=2HO+C^{12}H^4O^4.$$

If, on the contrary, orcine were the homologous compound, pyromoritannic acid ought to furnish, under the influence of air and ammonia, a compound corresponding to orcine, $C^{14}H^7NO^6$, as—

$$C^{12}H^6O^4+6O+NH^3=C^{12}H^5NO^6+4HO.$$

On comparing the properties and composition of pyromoritannic acid with those of pyrocatechine discovered by Zwenger, it is found that the two substances are identical.

Worthy of attention is the resemblance of the formula of pyromoritannic acid with those of pyrogallic and phenylous acid, for $C^{12}H^6+2O$=phenylous acid, $C^{12}H^6+4O$=pyromoritannic acid, and $C^{12}H^6+6O$=pyrogallic acid.

In the same manner as phenylous acid (the salicone of Stenhouse and Gerhardt) is produced from salicylic acid [$C^{14}H^6O^6$, salicylic acid$-2CO^2=C^{12}H^6O^2$, phenylous acid], and pyrogallic acid from gallic acid [$C^{14}H^6O^{10}$, gallic acid$-2CO^2=C^{12}H^6O^6$, pyrogallic acid], a product of decomposition of moritannic acid, which is formed from it by the action of concentrated sulphuric acid, and will be hereafter more particularly described, furnishes pyromoritannic acid. It is probable that Rochleder's bohcic acid, $C^{14}H^6O^8$, will likewise furnish pyromoritannic acid on dry distillation.

If we attempt to explain the formation of pyromoritannic acid from the formula at present admitted for moritannic acid, it might be done according to the following equation:—

$$C^{18}H^8O^{10}=C^{12}H^6O^4+C^2O^2+HO+4C.$$

Now if we take into consideration the formula, and the mode of formation of pyromoritannic acid, in which the production of phenylous acid is always evident, we must regard pyromoritannic acid as an acid which stands in the same relation to phenylous acid as the acetic to acetylous acid, that is as phenic acid.

According to Kolbe's view, benzoic acid is a conjugate acid consisting of the radical phenyle, $C^{12}H^5$, and oxalic acid, C^2O^3, HO. If phenic acid has an analogous constitution to benzoic acid, then it is oxalic acid conjoined with the hydrocarbon, $C^{10}H^5$. The rational formula of phenic acid would then be $C^{10}H^5$, C^2O^3, HO.

The ammonia salt of phenic acid cannot be prepared, otherwise it might be used to ascertain the composition of phenic acid. On distillation with anhydrous phosphoric acid, it would probably furnish the nitrile, C^2H^5N, which, judging from analogy, would be

the cyanide of phenylene, $C^2N + C^{10}H^5 : C^{12}H^5O^2$, $NH^4O - 4HO = C^{12}H^5N$.

On account of its want of stability, it was also impossible to prepare the potash salt of phenic acid, which would probably furnish, on electrolytic decomposition, phenylene, $C^{10}H^5$, just as the butyrate of potash gives C^6H^7.

St. Evre says, in his paper "On the Action of Chlorine upon Benzoate of Potash," that if it were possible to prepare phenic acid, we should be able to procure nicotine artificially. On distilling phenic acid with excess of alkali, the hydrocarbon, $C^{10}H^6$, ought to be formed for $C^{12}H^6O^4 - 2CO^2 = C^{10}H^6$; experiment however did not confirm this supposition, for on distilling phenic acid with excess of baryta, lime or alkali, the author obtained no hydrocarbon, but only unaltered phenic acid.

On distilling moritannic acid with excess of base, it likewise furnished only a liquid soluble in water, in which reagents showed the presence of phenic acid; it was impossible to obtain a hydrocarbon.

Phenic acid has consequently that property in common with phenylous acid, anisole, phenetole, phenamylole, and similar compounds, that it cannot be deprived of oxygen in the form of carbonic acid by being heated with an excess of alkali. Phenic acid however differs essentially from the above-mentioned substances, insofar as, hitherto at least, it has not been possible to prepare a base from it. No nitro-compound is formed by treatment with nitric acid, but only oxalic acid, which is coloured yellow by traces of a nitroacid.

When a few drops of a solution of phenic acid is added to a very dilute solution of perchloride of iron, a beautiful green colour is immediately produced, but no precipitate. On adding ammonia, the green passes into a beautiful red colour. This reaction is so sensitive, that the author recommends a solution of phenic acid as a test for peroxide of iron. If a liquid contain mere traces of peroxide of iron, which are scarcely indicated by sulphocyanide of potassium, there is formed, when the liquid has been previously mixed with tartaric acid and some ammonia, and so that the latter predominates, a distinctly perceptible violet colour immediately upon the addition of phenic acid; acetic acid converts this colour into a green one; ammonia restores the original violet. In this manner, by adding alternately ammonia and acetic acid, and employing not too dilute a solution of phenic acid, changes of colour are produced not inferior in beauty to those of the manganate and permanganate of potash. The test for iron is so sensitive, that a solution of phenic acid produces a bluish-violet stain upon filtering-paper on drying. The author calls attention to the property of phenylous acid, of striking a blue colour with a solution of the perchloride of iron. The salts of phenic acid, as also those of phenylous and pyrogallic acid, colour persalts of iron violet.

As is well known, a solution of gallic acid is employed as a test for alkalies and alkaline earths in water analyses, as a water which contains these bodies in small quantity soon acquires a green colour; a far more sensitive reagent than gallic acid is phenic acid, or rather

the phenate of the peroxide of iron. When a few drops of a very dilute aqueous solution of phenic acid, which has been mixed with a little perchloride of iron, are added to a water, which, like most of our potable waters, contain minute traces of alkalies, the liquid acquires, in the course of a few minutes, a deep blue colour.

Owing to the rapid alteration of colour which a solution of phenic acid in alkalies undergoes by exposure to the air, the author made an experiment to ascertain the absorptive power of a solution of phenic acid mixed with potash; he found that it absorbed oxygen just as well as pyrogallic acid.

Phenic acid furnishes, with a solution of chloride of lime or an alkaline hypochlorite, a black precipitate, and a supernatant black liquid; bichromate of potash behaves in the same manner. A current of sulphurous acid, passed through an aqueous solution of phenic acid, produces no alteration. By these reactions, phenic acid differs essentially from colourless hydroquinone.

Action of Oxidizing Agents upon Moritannic Acid.—When moritannic acid is treated with concentrated nitric acid, and the reddish-brown solution produced evaporated on the water-bath to expel the excess of nitric acid, yellowish-white prisms of a nitroacid are obtained, the potash salt of which detonates violently on being heated. The reactions show that this acid is identical with the oxypicric acid discovered by Erdmann.

When moritannic acid is treated with sulphuric acid and peroxide of manganese, as in the preparation of quinone from kinic acid, a violent disengagement of carbonic acid results, with production of formic acid; the moritannic acid is entirely destroyed. When moritannic acid is boiled with water and peroxide of lead, the brown peroxide turns reddish-yellow, the supernatant liquid becomes colourless on boiling, and contains a mere trace of lead. There was consequently formed an insoluble lead salt of a product of decomposition of moritannic acid, and which, on decomposition with sulphuretted hydrogen, exhibited properties proving its relation to the humous substances. When dry moritannic acid is triturated with dry peroxide of lead, the mass inflames during the operation, with scintillations and diffusion of a pungent odour. When rubbed together with chlorate of potash, moritannic acid detonates with the greatest violence.

An aqueous solution of moritannic acid, which had stood for about three months in a closed bottle, frequently exposed to sunlight, smelt and tasted of phenylous acid. The distillate from this solution gave the well-known reaction with perchloride of iron; wood, after being moistened with hydrochloric acid, was distinctly coloured blue by it. Hitherto the production of phenylous acid has only been observed by heat and the activity of the organism.

[To be continued.]

On the Preparation of Chelidonic Acid. By J. Hutstein.

The author has modified Lerch's process of preparing chelidonic acid by the employment of sulphuret of calcium. Lerch's state-

ment, that the full-blown plant contains most chelidonic acid, whilst that bearing buds furnishes more malic acid, was confirmed. The chelidonic acid is easily obtained by adding to every 2 lbs. of the expressed juice 1 drachm of nitric acid of 1·30 spec. grav., and then nitrate of lead, until no further precipitate is produced. The malate of lead remains in solution. The precipitate is collected upon linen, decomposed by pentasulphuret of calcium, when the lime salt is obtained crystallized upon evaporation. This is dissolved in 6 parts of boiling water, and readily converted into the ammonia salt by the addition of carbonate of ammonia.—*Archiv der Pharm.*, lxv. p. 23.

Experiments on the Pancreatic Fluid of the Calf.
By M. J. L. Lassaigne.

Since it has been shown that the pancreatic fluid extracted from the dog enjoys the remarkable property of making an emulsion with oil, and of causing its transformation into fatty acids, either at ordinary temperatures or at the temperatures of the bodies of mammalia, it has become matter of interest to submit to similar experiments the pancreatic fluid obtained from a large herbivorous animal, with the view of ascertaining if it acts in the same manner.

M. Colin, director of the anatomical department of the school of Alfort, having procured some of it by the method shown to him by M. Bernard, and which he had successfully put in practice with the dog, a small quantity was sent to M. Lassaigne, which he immediately examined.

The pancreatic fluid of the calf, which has an amber-yellow colour, is inodorous, transparent and limpid, and possesses a tolerably marked saline taste; when tested with reddened litmus-paper, it restores the blue tint. Heated, it becomes opalescent and turbid, and deposits some coagulated white flakes, which attach themselves to the sides of the vessel in which the experiment is made.

The small quantity at the author's disposal not permitting of a direct analysis, he thought it right to examine, in concert with M. Colin, the action which it exercises on oils.

For this purpose he divided it into several portions in glass tubes, and added to each portion a drop of pure olive oil. The agitation to which he subjected the tubes formed no emulsion, the oil separating speedily, and floating on the top.

The prolongation of the experiment did not produce any effect, even after eight hours of contact at a temperature of 60° F., the oil having remained neutral and the liquid preserving its primitive alkalinity. Subsequently exposing these same tubes in a salt-water bath to 100° F., and keeping up this temperature for fourteen hours, produced no change in the properties of the oil, or in those of the pancreatic juice subjected to the experiment.

This result is opposed to that obtained from the pancreatic juice of the dog. Is it constant in the herbivorous animal, or is it an exceptional occurrence due to an alteration in the pancreatic juice of the animal, caused by the painful operation to which it had been

subjected? The author does not admit the latter hypothesis, seeing that the animal survived, and did not appear to suffer in health.—*Journ. de Pharm.*, March 1851; and *Monthly Journal of Medical Science*, May 1851.

✓ *On the Composition of the Oxide of Bismuth, and the Equivalent of this Metal. By* R. Schneider.

Hitherto the results of the experiments made in 1814 by Lagerhjelm have been generally admitted as proving the composition of the oxide of bismuth, and consequently the equivalent of this metal; he found that 100 parts of bismuth furnished, on oxidation with nitric acid, evaporation to dryness and calcination, 111·275 oxide of bismuth. It is upon this single datum that the equivalent 1330·37 for bismuth has been established. L. Gmelin, however, who has more recently experimented on the composition of oxide of bismuth, found very different results, and has stated that the equivalent of the metal ought to be reduced at least to 1312·5. It became therefore important to submit the subject to a fresh examination, which has been done by the author.

The method which he followed is identical with that of Lagerhjelm; but it was carried out with the most minute precautions, both as regards the purification of the bismuth submitted to oxidation, and in guarding against all chances of loss during the solution of the metal in nitric acid, evaporation to dryness and calcination, which operations were executed in a glass flask. The results obtained by the author appear to be most trustworthy. The mean result of eight experiments gave, for the composition of the oxide of bismuth—

Bismuth	89·655
Oxygen	10·345

Calculating from this the equivalent of bismuth, admitting for the oxide the formula Bi^2O^3, we obtain the number 1299·97, or simply 1300, which confirms the announcement made by Gmelin. Bismuth appears to belong to the numerous group of simple bodies the equivalent of which is an exact multiple of that of hydrogen. Hydrogen being represented by 1, bismuth would be by 104. It must however be observed, that this almost absolute coincidence may after all only be accidental; for with so high an equivalent even the sum of the whole numbers can scarcely be considered as perfectly certain. —Poggendorff's *Annalen*, lxxxii. p. 303.

✓ *On the Compound Ammonias. By* A. Wurtz.

[Continued from p. 228.]

Æthylamine.—This is prepared in the same way as methylamine, by decomposing the muriate of æthylamine with caustic lime; it is more easily obtained, being liquid at the ordinary temperature. The receiver is cooled with ice or with a refrigerating mixture.

Properties.—It forms a light, very mobile, perfectly transparent

liquid, which boils at 18°·7 C. When poured upon the hand, it is mediately volatilized, and produces a lively sensation of cold. It does not become solid in a mixture of æther and carbonic acid. Its specific gravity is 0·6964 at 8°. The density of the vapour was determined by M. Izarn, in Regnault's laboratory, by means of a new apparatus. The results are given in the following table, together with the densities of methylamine, determined by M. Izarn in the same manner. The following are the results:—

I. Methylamine. 0·402 grm. substance. Calculated density, 1·0733 for 4 vols. of vapour.

Volume.	Temperature.	Pressure.	Density.
290·2 cub. cent.	7·40 Cent.	763·56 millims.	1·0951
230·4	7·40	952·73	1·1055
350·0	26·91	683·76	1·0840
290·2	26·86	822·09	1·0873
230·4	26·78	1029·20	1·0935
350·0	36·32	706·19	1·0823
290·2	36·30	849·48	1·0849
350·0	43·41	723·77	1·0800
290·2	43·41	870·32	1·0832

II. Æthylamine. 0·627 grm. substance. Calculated density, 1·5568 for 4 vols. of vapour.

Volume.	Temperature.	Pressure.	Density.
350·0 cub. cent.	27·36 Cent.	729·91 millims.	1·5867
290·2	27·36	875·91	1·5940
350·0	35·93	753·30	1·5803
290·2	35·95	904·19	1·5880
230·4	35·84	1128·00	1·6027
350·0	43·36	773·04	1·5767
290·2	43·39	928·14	1·5840
230·4	43·97	1161·10	1·5977
350·0	48·75	787·13	1·5747
290·2	48·98	946·02	1·5813
230·4	49·08	1182·20	1·5943
350·0	55·23	803·86	1·5728
290·2	55·28	966·33	1·5782
230·4	55·13	1206·25	1·5917

A. Methylamine. 0·402 grms. substance.

Volume.	Temperature.	Pressure.	Density.
350·0 cub. cent.	26·91 Cent.	683·76 millims.	1·0840
...	36·32	706·19	1·0823
...	43·41	723·77	1·0800
290·2	7·40	763·56	1·0951
...	26·86	822·09	1·0873
...	36·30	849·48	1·0849
...	43·41	870·32	1·0832
230·4	7·40	952·73	1·1055
...	26·78	1029·20	1·0935

B. Æthylamine. 0·627 grm. substance.

Volume.	Temperature.	Pressure.	Density.
350·0 cub. cent.	27·36 Cent.	729·91 millims.	1·5867
...	35·93	753·30	1·5803
...	43·36	773·04	1·5767
...	48·75	787·13	1·5747
...	55·23	803·86	1·5728
290·2	27·36	875·91	1·5940
...	35·95	904·19	1·5880
...	43·39	928·14	1·5840
...	48·98	946·02	1·5813
...	55·28	966·33	1·5782
230·4	35·84	1128·00	1·6027
...	43·97	1161·20	1·5977
...	49·08	1182·10	1·5943
...	55·13	1206·25	1·5917

The last tables, A, B, contain the same numbers as I. and II., only arranged in a different order. The first, I. and II., exhibit the results as they were obtained, and show the deportment of the gas when at the same temperatures the volume is diminished with increasing pressure. It is evident from them that the density increases with the pressure.

In the tables A and B are contained the results which were found for the same volumes with nearly the same pressure, but at different temperatures; in this case we likewise observe the ordinary behaviour of gases; the density diminishes with the increase of temperature.

All the above-mentioned numbers are greater than the theoretical densities, but they come the closer to the latter the more suitable the conditions. In the case of methylamine it is very near; and it would certainly have been completely attained if the temperature could have been further increased or the pressure further diminished; for even at tolerably low temperatures, it is seen, that, with a suitable dilution, the gas approached the point at which it would have followed Mariotte's law like a permanent gas.

It is moreover remarkable, that æthylamine, which boils between 18° and 19° Cent. under a pressure of 760 millimetres, has so low a density at 27°. According to some experiments on the elasticity of its vapour, its boiling-point, under a pressure of 876 millims., falls to 73°. At this temperature, which is situated only 4° below that above mentioned, it would only have a density of 1·5940, which differs from the theoretical one by 0·037.

Æthylamine has a strong ammoniacal odour, and is as caustic as potash; one drop placed on the tongue immediately produces inflammation with a burning pain; it instantly turns red litmus-paper blue, and saturates acids just like ammonia; held near muriatic gas, it gives off dense white fumes. One drop of acid let fall into the liquid alkaloid produces a hissing noise. It mixes with water in every proportion, and imparts to it a certain viscosity, which distinguishes this solution from one of ammonia. Æthylamine, when

ignited, burns with a yellowish flame. Towards salts of the metallic oxides it behaves, with scarcely a single exception, like methylamine; however, the precipitate produced in salts of the oxide of copper is less quickly dissolved by æthylamine. Chloride of platinum is not precipitated immediately by a moderately-concentrated solution. The solubility of alumina in æthylamine is very remarkable; it behaves like potash towards alum, and if it were possible to prepare it on a large scale, it would answer much better than potash for separating iron from alumina. Æthylamine expels ammonia from its compounds; when muriate of ammonia is mixed with a large excess of æthylamine, the muriate of æthylamine is left on evaporation. When a mixture of æthylamine and ammonia, the former in excess, is half-neutralized with sulphuric acid, there is left on evaporation sulphate of æthylamine, which contains but a mere trace of ammonia. We may therefore employ, for the separation of æthylamine from ammonia, the method of partial saturation proposed by Liebig for the separation of the volatile fatty acids.

Analysis of anhydrous æthylamine:—

Carbon	53·61	4 =	24	53·33
Hydrogen	15·60	7	7	15·55
Nitrogen	31·45	1	14	31·12

Behaviour at a high temperature.—The gas is passed through an incandescent tube filled with fragments of porcelain; the products are passed through water containing peroxide of mercury in suspension, in order to retain the prussic acid. The gases were hydrogen, a comparatively small quantity of carburetted hydrogen and a trace of nitrogen. The water with which these gases had been washed contained a large amount of ammonia, and the greater portion of the peroxide of mercury was converted into cyanide.

Bichlorinated Æthylamine, $C^4 \frac{H^5}{Cl^2} N$.—Chlorine acts instantly upon æthylamine; muriate of æthylamine and bichlorinated æthylamine are formed, with evolution of heat and the elimination of a small quantity of nitrogen, $2C^4 H^7 N + 3Cl = C^4 H^7 N, ClH + C^4(H^5 Cl^2)N$. An excess of chlorine converts the bichlorinated æthylamine into a solid crystalline substance.

It forms a yellowish very mobile liquid, with a penetrating odour, which excites coughing and tears. It boils at 91° C., and distils over, condensing into a clear liquid, which deposits in the course of a few days some minute colourless spangles. When its vapour is over-heated in a tube, it detonates, without however fracturing the tube. It is decomposed by ammonia, and resolved by potash into chloride of potassium, acetic acid and ammonia, $C^4 H^5 Cl^2 N + 3KO + HO = KO, C^4 H^3 O^3 + NH^3 + 2ClK$. This decomposition is extremely interesting, as in this case the base æthylamine is converted into its corresponding acid, acetic acid. The bichlorinated æthylamine furnished on analysis—

Carbon	21·12	..	4 =	24	21·05
Hydrogen	4·51	..	5	5	4·38
Chlorine	62·07	62·50	2	71	62·28
Nitrogen	..	..	1	14	12·29

Hofmann has pointed out, that, in the chlorinated derivatives formed by the substitution of the hydrogen in aniline, the basic properties decrease in proportion as the chlorine equivalents increase; the bichlorinated and trichlorinated anilines are still bases, although their basic characters are less marked than those of aniline; but the bichlorinated æthylamine has already lost all basic properties. It may therefore be assumed, that in the bichlorinated æthylamine the chlorine has taken the place of the two basic hydrogen equivalents of the ammonia; whilst the æthylamine itself, occupying the place of the third equiv. of hydrogen of the ammonia, has remained intact.

Bibrominated Æthylamine.—Bromine is poured gradually into a concentrated solution of æthylamine, which is cooled with ice; a violent reaction takes place, which is terminated when the bromine is no longer decolorized in the neutral liquid; an oily liquid separates in small quantity; a greater portion remains dissolved in the liquid, from which it can be obtained by agitation with æther. On evaporation, an orange-red residue is left, from which any excess of bromine can be removed by dilute caustic potash. It is heavier than water, has a pungent odour resembling that of the preceding chlorinated substance, and has probably the same composition.

Biniodated Æthylamine, $C^3 H^5 I^2 N$(?).—Iodine converts æthylamine into a thick blackish-blue liquid. Hydrogen is replaced by iodine, but the product differs considerably in its properties from the chlorinated body. On distillation, iodine is given off; when the temperature is increased, a dark brown liquid passes over, and there is left a residue of carbon. Alcohol and æther dissolve this substance; caustic potash does not decompose it immediately, but only after a couple of days, forming iodide of potassium, iodate of potash, and a somewhat considerable amount of a yellow crystalline substance, which dissolves slightly in water, more readily in alcohol, from which solution it does not crystallize. This iodated æthylamine furnished no definite results on analysis; it appears at least not to be the compound corresponding to iodoform; but, according to the following analyses, which do not agree very closely, a mixture of different substances with biniodated æthylamine:—

Carbon	8·28	7·90	8·33	4	= 24	8·13
Hydrogen	2·03	1·98	1·80	5	5	1·69
Iodine	..	..	86·38	2	252	85·42
Nitrogen.....	..	..	..	1	14	4·76

Hydrochlorate of Æthylamine, $C^4 H^7 N, HCl$, is obtained either by decomposing cyanuric æther in the same apparatus as that employed for the preparation of the hydrochlorate of methylamine, or by decomposing cyanic æther by potash. The reaction commences immediately at the ordinary temperature, with considerable disengagement of heat. The decomposition is most advantageously effected in a flask with a ground stopper, which latter is tightly fitted in, and the flask cooled. In five minutes the reaction is complete. The flask, which contains only carbonate of potash and æthylamine, is heated to boiling to expel the latter, which is passed

into a receiver containing some water, and therein saturated with some hydrochloric acid; it is then evaporated to dryness, and the residue dissolved in boiling alcohol, from which the hydrochlorate of æthylamine crystallizes in the form of broad laminæ.

When the crystals have been perfectly dried *in vacuo*, they fuse at 76°, and are perfectly liquid at 80° C. On cooling, the substance forms a crystalline, semitransparent, fissured mass. When the muriate of æthylamine is heated still more, it evaporates, and begins to boil between 315° and 320°. When cold, the mass is now turbid, and no longer crystalline. This modified salt only became liquid at 260°. The hydrochlorate of æthylamine is deliquescent; sometimes beautifully-striated prisms are obtained from an aqueous solution. On treatment with potassium amalgam, hydrogen is liberated and æthylamine dissolved. Analysis:—

Carbon	28·93	29·52	4 =	24·0	29·44
Hydrogen	9·94	9·99	8	8·0	9·81
Chlorine	43·58	..	1	35·5	43·55
Nitrogen	..	..	1	14·0	17·20

Hydrochlorate of Æthylamine and Platinum, $C^4 H^8 NCl, PtCl^2$, is obtained by adding alcohol to a mixture of solutions of hydrochlorate of æthylamine and chloride of platinum. The precipitate is dissolved in boiling water, from which it separates on cooling in beautiful dark yellow prisms, which furnished on analysis—

Carbon	9·48	4 =	24·0	9·55
Hydrogen	3·31	8	8·0	3·18
Chlorine	42·65	3	106·5	42·41
Platinum	39·00	1	98·6	39·26
Nitrogen	..	1	14·0	5·60

Hydrochlorate of Æthylamine and Mercury, $C^4 H^7 N, HCl, HgCl$. —This compound is obtained by mixing equivalents of bichloride of mercury and hydrochlorate of æthylamine. It crystallizes more readily than the corresponding salt of methylamine. Analysis gave—

Carbon	11·01	4 =	24	11·01
Hydrogen	3·88	8	8	3·67
Chlorine	32·71	2	71	32·56
Mercury	..	1	101	46·33
Nitrogen	..	1	14	4·43

Hydrochlorate of Æthylamine and Gold, $C^4 H^7 N, HCl + AuCl^3$, is obtained like the preceding salt, and forms golden prisms soluble in water, alcohol and æther. Analysis gave—

Carbon	6·21	4 =	24	6·20
Hydrogen	2·38	8	8	2·06
Chlorine	36·83	4	142	36·69
Gold	51·39	1	199	51·42
Nitrogen	..	1	14	3·63

Carbonate of Æthylamine is obtained by distilling a mixture of dry carbonate of lime and hydrochlorate of æthylamine. The va-

pours which first pass over condense into a powder, those which follow into a liquid. According to analysis, the composition of the solid portion of the distillate, dried by quickly pressing it between blotting-paper, is not constant as regards the carbonic acid. The salt is strongly alkaline, the odour ammoniacal; at the ordinary temperature it gives off fumes, which turn red litmus-paper blue; it dissolves carbonate of copper and carbonate of zinc.

Anhydrous Carbonate of Æthylamine, $C^4 H^7 N, CO^2$, was procured by passing a current of dry carbonic acid into a receiver containing anhydrous æthylamine; the matrass was cooled considerably; the liquid æthylamine became converted into a snow-white mass. The solution of this salt does not precipitate chloride of barium immediately, but only after some time, or when it has been heated. Analysis gave the following composition:—

Carbon	44·37	5 =	30	44·77
Hydrogen	10·65	7	7	10·44
Nitrogen	..	1	14	20·89
Oxygen	..	2	16	23·90

Hydrosulphate of Æthylamine is readily obtained when sulphuretted hydrogen is passed into a flask containing anhydrous æthylamine, and placed in ice. Before introducing the sulphuretted hydrogen, the flask should be filled with hydrogen. This salt fuses readily and is volatile. The fused mass solidifies on cooling into beautiful crystals, which appear to be oblique prisms with rectangular bases. The vapour of this salt is inflammable. It becomes yellow in the air, attracts moisture, and deliquesces into yellow drops. The solution dissolves recently-precipitated sulphuret of antimony, forming a colourless liquid, which deposits an orange powder on evaporation.

Sulphate of Æthylamine is deliquescent, not crystalline, very easily soluble in alcohol, and dries *in vacuo* to a gum-like mass. This solubility in alcohol furnishes a ready method of separating æthylamine from methylamine.

Nitrate of Æthylamine, formed by saturating the base with nitric acid, separates from the concentrated syrupy solution in very deliquescent plates. If the syrupy solution is heated too strongly, nitrous fumes are given off, and the decomposition then proceeds of itself further. The gases evolved are inflammable, and burn, like nitrogenous compounds, with a yellow flame.

Æthylamine and Protochloride of Platinum furnishes $2Pt Cl^2, 2C^4 H^7 N$, which is the compound corresponding to the green salt of Magnus. It separates immediately on mixing the two substances, with evolution of heat, as a chamois-coloured powder. It is insoluble in water, and furnished on analysis—

Carbon	13·51	8 =	48·0	13·40
Hydrogen	4·02	14	14·0	3·90
Platinum	54·75	2	197·2	55·05
Nitrogen	..	2	28·0	7·81
Chlorine	..	2	71·0	19·84

The compound analogous to Reiset's salt, $C^4 H^7 N, C^4 (H^6 Pt) N$

$+HCl+2HO$, is obtained on heating the preceding compound with an excess of æthylamine. In order to lose no æthylamine, the operation is conducted in sealed tubes in a water-bath. When the chamois-coloured salt has disappeared, there frequently remains a black powder, which detonates on the application of heat, and probably corresponds to fulminating platinum. On evaporating the filtered liquid, beautiful colourless crystals are obtained, which are pretty soluble in water, but sparingly so in alcohol. They are the hydrochlorate of a new platinum base, as evident from the following analysis:—

Carbon	20·2	20·1	8 =	48·0	19·82
Hydrogen	7·3	7·0	16	16·0	6·61
Platinum	40·2	40·2	1	98·6	40·72
Chlorine	14·4	..	1	35·5	14·66
Nitrogen	..	..	1	28·0	11·56
Oxygen	..	..	2	16·0	6·63

The sulphate of this base, $C^4H^7N+C^4(H^6Pt)N+SO^4H$, which corresponds to the preceding salt, is obtained by decomposing the latter with sulphate of silver in large colourless crystals. It gave on analysis—

Carbon	20·12	8 =	48·0	20·22
Hydrogen	6·04	13	13·0	5·97
Platinum	41·40	1	98·6	41·67
Nitrogen	..	2	28·0	11·83
Sulphuric acid	..	1	49·0	20·31

The base which is produced in the action of æthylamine upon the protochloride of platinum corresponds to the first of M. Reiset's bases $=NH^3$, NH^2Pt. It has likewise a similar constitution, and is produced by the union of two molecules of æthylamine in which 1 equiv. of hydrogen has been replaced by 1 equiv. of platinum. The following formulæ express the constitution of a series of evidently-corresponding bases:—

1. Reiset's base.

Platinamine, *Wurtz**.	Platinomethylamine.	Platinoæthylamine.
NH^3 $N\left\{\begin{matrix}H^2\\Pt\end{matrix}\right.$	$N\left\{\begin{matrix}H^2\\C^2H^3\end{matrix}\right.$ $N\left\{\begin{matrix}H\\Pt\\C^2H^3\end{matrix}\right.$	$N\left\{\begin{matrix}H^2\\C^4H^5\end{matrix}\right.$ $N\left\{\begin{matrix}H\\Pt\\C^4H^5\end{matrix}\right.$

2. Reiset's base.

Platinia.	Platinomethylia.	Platinoæthylia.
$N\left\{\begin{matrix}H^2\\Pt\end{matrix}\right.$	$N\left\{\begin{matrix}H\\Pt\\C^2H^3\end{matrix}\right.$	$N\left\{\begin{matrix}H\\Pt\\C^4H^5\end{matrix}\right.$

In these compounds the platinum evidently replaces hydrogen; they have therefore all the most perfect analogy with each other, and the same general formula, NR^3.

* Wurtz's name of *platinamine* is likely to lead to confusion with Gerhardt's *platinammine*. Reiset's first base is Gerhardt's *diplatosammine*; the second is Gerhardt's *platosammine*.

Oxalate of Æthylamine, $C^4 H^7 N, C^2 HO^4$.—Æthylamine is mixed with oxalic acid; on evaporating the solution, right rhombic prisms are obtained, which furnished—

Carbon	40·28	6 =	36	40·00
Hydrogen	9·01	8	8	8·88
Nitrogen	15·58	1	14	15·55
Oxygen	..	4	32	55·57

Æthyloxamide, $C^6 H^6 NO^2$.—When oxalate of æthylamine is heated, it is readily decomposed, and loses 2 equivs. water, $C^6 NO^4 H^8 = C^6 H^6 NO^2 + H^2 O^2$. When oxalate of æthylamine is mixed with an excess of oxalic acid and fused at 180° C., a small quantity of æthyloxamic acid is formed. Æthyloxamide is most easily obtained by acting with æthylamine upon oxalic æther; alcohol is formed, and æthyloxamide deposited—

$$C^4 H^5 O, C^2 O^3 + C^4 H^7 N = C^4 H^6 O^2 + C^2 O^2, C^4 H^6 N.$$

Æthyloxamide is more soluble in alcohol than in water, from which latter it crystallizes in beautiful needles. It is volatile, and condenses in woolly crystals on the surface of a cold body.

Potash resolves it into oxalic acid and æthylamine. Anhydrous phosphoric acid carbonizes it. On analysis it furnished—

Carbon	49·83	6 =	36	50·00
Hydrogen	8·55	6	6	8·33
Nitrogen	..	1	14	19·44
Oxygen	..	2	16	22·23

Acetate of Æthylamine.—When the vapours of æthylamine are passed into a flask containing crystallizable acetic acid, and surrounded by ice, a dazzling white crystalline mass of acetate of æthylamine is obtained. Phosphoric acid has a violent action upon it, but it does not yield any product corresponding to acetonitryle.

Æthylacetamide, $C^8 H^9 NO$, is obtained when a mixture of acetic æther and aqueous æthylamine is evaporated, at first on the water-bath, and then *in vacuo*. It remains liquid, and is volatile; boils at 200° C., when it experiences but a very slight decomposition. Potash resolves it into æthylamine and acetic acid; anhydrous phosphoric acid carbonizes it.

[To be continued.]

On the Acrid Substance of the Root of Iris tuberosa.

By M. Landerer.

The acrid principle of *Iris tuberosa* is volatile. It separates upon the water distilled from the root as a stearoptene, in nacreous scales. When extracted from the root by means of æther, this on evaporation furnishes an acrid extract, which, upon being rubbed upon the skin, produces considerable inflammation.—*Archiv der Pharm.*, lxv. p. 302.

PROCEEDINGS OF SOCIETIES.

Royal Society. May 22, 1851.

Additional Observations on the Diffusion of Liquids. By Professor Graham.

The experiments detailed in this paper were conducted with the same apparatus and in the same manner as those described in the author's two former papers on this subject*. The diffusion is generally made from four different proportions of each solution, so as to exhibit pretty fully the character of the salt in reference to this property. The salts operated upon are of two bases only, potash and soda, but the acids are considerably varied, so as to include the hydrates, carbonates, sulphates, sulphites, hyposulphites, sulphovinates, oxalates, acetates and tartrates of these bases.

The times chosen for the corresponding potash and soda salts, with the view of obtaining equal diffusions, are always in the proportion of 1·4142 to 1·7320, that is, as the square root of 2 to the square root of 3. Eight cells were diffused of the 1 and 2 per cent. solutions, and four cells of the 4 and 8 per cent. solutions. The salts are always taken anhydrous.

Diffusion of hydrate of potash in 4·04 days at 63°·4: two cells.

	Grs.	Ratio.
From 1 per cent. solution	6·56	1·022
„ 2 „ „	12·84	2·
„ 4 „ „	25·04	3·900
„ 8 „ „	52·24	8·137

Diffusion of hydrate of soda in 1·937 days at 63°·3: two cells.

	Grs.	Ratio.
From 1 per cent. solution	5·81	1·048
„ 2 „ „	11·09	2·
„ 4 „ „	20·86	3·765
„ 8 „ „	40·44	7·30

The nearest approach to equality of diffusion in the hydrates of potash and soda is exhibited by the 1 per cent. solutions, which are as 6·56 to 5·81, or as 100 to 88·57.

Diffusion of carbonate of potash in 8·083 days, double the time of hydrate of potash, at 63°·7: two cells.

	Grs.	Ratio:
From 1 per cent. solution	6·13	1·028
„ 2 „ „	11·92	2·
„ 4 „ „	22·88	3·839
„ 8 „ „	45·44	7·624

Diffusion of carbonate of soda in 9·875 days, double the time of hydrate of soda, at 63°·4: two cells.

	Grs.	Ratio.
From 1 per cent. solution	6·02	1·028
„ 2 „ „	11·70	2·
„ 4 „ „	21·42	3·661
„ 8 „ „	39·74	6·792

* Chem. Gaz., vol. viii. p. 38, and p. 186 of the present volume.

The diffusion of carbonate of potash appears similar to that of the carbonate of soda in the 1 and 2 per cent. solutions, but they diverge in 4 and 8 per cent. solutions.

Diffusion of sulphate of potash in 8·083 days at 60°·3: two cells.

	Grs.	Ratio.
From 1 per cent. solution	6·16	1·062
„ 2 „ „	11·60	2·
„ 4 „ „	22·70	3·914
„ 8 „ „	43·92	7·572

Diffusion of sulphate of soda in 9·875 days at 59°·9: two cells.

	Grs.	Ratio.
From 1 per cent. solution	6·33	1·055
„ 2 „ „	12·00	2·
„ 4 „ „	21·96	3·66
„ 8 „ „	41·38	6·896

The following results of the diffusion of various salts from the 2 per cent. solution were obtained; the times being always 8·083 days for the potash salts and 9·875 days for the soda salts:—

	Grs.	Ratio.
Sulphate of potash at 60°·3 (as above)...	11·60	100·
Sulphite of potash at 59°·5	11·63	100·26
Sulphite of soda at 59°·6	11·83	101·72
Hyposulphite of potash at 59°·8	12·37	106·44
Hyposulphite of soda at 59°·9	11·89	101·10
Sulphovinate of potash at 59°·8	12·60	108·62
Sulphovinate of soda at 59°·6	13·03	
Tartrate of potash at 59°·9	10·96	
Tartrate of soda at 59°·6	10·65	
Carbonate of potash at 59°·9	10·73	
Carbonate of soda at 59°·6	10·65	

Diffusion of oxalate of potash in 8·083 days at 59°·9: two cells.

	Grs.	Ratio.
From 1 per cent. solution	6·20	1·019
„ 2 „ „	12·17	2·
„ 4 „ „	23·04	3·789
„ 8 „ „	42·82	7·042

The oxalate of potash corresponds closely with sulphate of potash.

The diffusion from the 1 per cent. solution of oxalate of soda at 59°·9, gave 6·24 grs. in 9·875 days, or a nearly equal diffusate to that of the oxalate of potash.

Diffusion of acetate of potash in 8·08 days at 60°·3: two cells.

	Grs.	Ratio.
From 1 per cent. solution	6·44	1·028
„ 2 „ „	12·52	2·
„ 4 „ „	23·44	3·744
„ 8 „ „	47·26	7·549

The acetate is found to exceed sensibly the sulphate and oxalate of potash in diffusibility, at the preceding temperature.

Diffusion of acetate of soda in 9·87 days at 59°·6: two cells.

	Grs.	Ratio.
From 1 per cent. solution	6·67	1·070
„ 2 „ „	12·46	2·
„ 4 „ „	25·04	4·019
„ 8 „ „	48·04	7·711

The diffusion of acetate of soda presents a general parallelism to that of acetate of potash for the times chosen, the temperatures of the two series of experiments differing only 0·7 degree.

The salts of potash and soda of the same base appear therefore to give approximately equal amounts of diffusate, when diffused for the two different times chosen, with the remarkable exception of the hydrates of these two bases. The relation is most observable in the small proportions of salt, or weak solutions, such as the 1 and 2 per cent. solutions. The soda salts, as a general rule, fall off in diffusibility in the higher proportions as compared with potash salts.

The double tartrate of potash and soda was observed to undergo decomposition in diffusion, the tartrate of potash separating from the tartrate of soda from the higher diffusibility of the former.

Royal Institution.

June 13, 1851. (The Duke of Northumberland, President, in the Chair.) The following paper was read:—

"On Schönbein's Ozone," by Professor Faraday.

The object of the speaker was to give a brief account of the present state of this subject, taking at the same time notice of the ancient facts which belong to it, and the high hopes of progress which it offers for the future. Ozone is produced when the electrical brush passes from a moist wooden point into the atmosphere, and indeed in almost every case of electrical discharge in the air; or when water is electrolized, as in the case of a dilute solution of sulphuric acid or sulphate of zinc; or when phosphorus acts at common temperatures on a moist portion of the atmosphere. For the latter case, take a piece of clean phosphorus, about half an inch long, which has been recently scraped; put it into a clean two-quart bottle, at a temperature of about 60° F., with as much water as will half cover the phosphorus; close the mouth slightly, so that if inflammation take place, no harm may happen; and leave it. The formation of ozone will quickly occur, being indicated by the luminous condition of the phosphorus and the ascent of a fountain-like column of smoke from it. In less than a minute the test will show ozone in the air of the bottle; in five or six hours it will be comparatively abundant; and then the phosphorus being removed and the acids formed at the time washed out, the bottle may be closed, and made use of when required for experiments.

The test for ozone is as follows:—1 part of pure iodide of potassium, 10 parts of starch and 200 parts of water are to be boiled together for a few moments. A little of this preparation, placed on writing-paper with a brush, being introduced into the ozone atmo-

sphere, is rendered instantly blue from the evolution of iodine; or if bibulous paper be dipped into this solution, and then dried, it forms Schönbein's ozonometric test; for a slip being introduced dry into an atmosphere supposed to contain ozone, after remaining there a longer or shorter time, on being removed and then moistened, instantly becomes more or less deeply blue if ozone be present.

Ozone, when obtained by the three very different processes described, is identical in every respect; its properties are as follow:— 1. It is a gaseous body, of a very peculiar odour; when concentrated, the odour approaches to that of chlorine; when diluted, it cannot be distinguished from what is called the electric smell. 2. Atmospheric air strongly charged with it renders respiration difficult, causes unpleasant sensations, and produces catarrhal effects (by acting powerfully on the mucous membranes). Such air soon kills small animals, as mice, placed in it; so that ozone in its pure state must be highly deleterious to the animal œconomy. 3. It is insoluble in water. 4. Like chlorine, bromine and the metallic peroxides, it is a powerful electromotive substance. 5. It discharges vegetable colours with a chlorine-like energy. 6. It converts phosphorus ultimately into phosphoric acid; it combines with chlorine, bromine and iodine; it does not unite with nitrogen under ordinary circumstances, but does when lime-water is present, and nitrate of lime is formed, from which nitre may be readily obtained. 7. At common, and even low temperatures, it acts powerfully upon most metallic bodies, producing the highest degree of oxidation they are capable of. Lead, and even silver, is carried at once to the state of peroxides; arsenic and antimony produce arsenic and stibic acids. 8. It transforms many of the lower oxides into peroxides; thus the hydrate of the oxides of lead, cobalt, nickel and manganese become in it peroxides; the basic oxide of silver undergoes the same change. 9. It decomposes rapidly the solid and dissolved protosalts of manganese, the hydrated peroxides of the metal being formed and the acid of the salts evolved. 10. It decomposes the solution of the tribasic acetate of lead, the peroxide of that metal and the ordinary acetate being formed. 11. It rapidly converts the protosalts of iron and tin into persalts. 12. It destroys many hydrogenated gaseous compounds; the combinations of hydrogen with sulphur, selenium, phosphorus, iodine, arsenic and antimony are thus affected. It appears to unite chemically with olefiant gas in the manner of chlorine. 13. It instantly transforms the sulphurous and nitrous acids into the sulphuric and nitric acids, and the sulphites and nitrites into sulphates and nitrates. 14. It changes many metallic sulphurets (as those of lead and copper) into sulphates. 15. It decomposes many iodides in their solid and dissolved state. By its continued action, iodide of potassium becomes converted into iodate of potash. 16. It changes both the crystallized and dissolved yellow prussiate of potash into the red salt, potash being evolved. 17. It produces oxidizing effects upon most organic compounds, causing a variety of chemical changes; thus guaiacum is turned blue by it. From the

above enumeration it would appear that ozone is a most ready and powerful oxidizer, and in a great number of cases acts like Thénard's peroxide of hydrogen, or chlorine, or bromine.

A number of the actions of this body, such as the bleaching of indigo and litmus, the peroxidation of metals, the conversion of sulphurets into sulphates, &c., were shown, to illustrate the chlorine-like action of the ozone; and many illustrations supplied by M. Schönbein himself were exhibited.

With respect to the nature of this body, the two chief ideas are,—that it is a compound of oxygen analogous to the peroxide of hydrogen, or that it is oxygen in an allotropic state, *i. e.* with the capability of immediate and ready action impressed upon it. When an ozonized atmosphere is made as dry as possible, and then sent through a red-hot tube, the ozone disappears, being converted apparently into ordinary oxygen, and no water or any other result is produced. This agrees with the known fact, that heat prevents the formation of ozone, and also with the idea that ozone is only oxygen in an allotropic state. To show that heat prevents the formation of ozone, a little voltaic battery was associated with a fine platina-wire helix, insulated, and connected with the electrical machine; at first the circuit between the battery and the helix was left incomplete; and then, on working the machine, the brush thrown off from the helix affected the test-paper before described by the ozone in it; but when the connexion was complete, so that the helix was ignited, then the electrical brush from it had no power of producing any effect of ozone.

The speaker described the presence of ozone in the atmosphere, the mode of testing its presence, and the probable effects it produced there. He referred to Schönbein's recent experiments on the insulation of the oxygen of the air and the peculiar effects produced by this action. He showed by experiments the more recent results of the association of oxygen by light with oil of turpentine and other bodies, and the production of bleaching compounds vieing with the hypochlorite of lime in energy. He made it manifest by experiment, that when æther-vapour is mixed with air, and a hot platina wire or glass rod introduced, the æther, in becoming partially oxidized to produce acid, also produces ozone, the results bleaching indigo powerfully; and he stated that sulphurous acid, æther, tartaric acid, and many other substances, which, being first mixed with air or oxygen, were then exposed to sunlight, exerted bleaching powers often of a very high degree.

The evening concluded with the expression of certain theoretical expectations, or rather possibilities, which were put forth as indicating the probable fertility and importance of the subject, and fitted to excite such philosophers as were engaged in the consideration of the physical qualities of the particles of matter, to examine how far the phænomena of ozone might be carried onward in the illustration and extension of their researches.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Astringent Principle of Kino. *By* Dr. T. Gerding.

Kino is the inspissated juice of various exotic plants, and is employed in medicine on account of its considerable amount of tannin. Four kinds of this product are distinguished; they all form brown, dry, shining masses or grains, and are named after the country from whence they are derived, as African, Asiatic, New Holland and American. It is not known for certain from what plants these drugs are obtained.

African Kino (*Kino verum* or *Kino Gambiense*) is said to be obtained from *Pterocarpus erinaceus*, Lam. (*Pt. Senegalensis*, according to Hooker). When the bark of this African tree is injured, an abundant exudation of sap occurs, which when dry furnishes the above-named product.

Asiatic Kino (*Kino Ostindicum* or *Kino orientale*) is considered to be the inspissated juice, altered by the long action of sunlight, of *Butea frondosa*, Roxb. (*Erythrina monosperma*, Lam.), and also of *Pterocarpus marsupium*.

The New Holland Kino is said to be derived from *Eucalyptus resinifera*, White.

American Kino (*Kino occidentale*, and likewise called *American* and *spurious extract of Ratanhia*) is the extract obtained from a decoction of the fibrous wood of *Cocoloba uvifera*.

This product occurs in irregular, brittle, brown, opake fragments, which are generally coated externally with a reddish dust, have a resinous fracture, and possess a bitter astringent taste. The New Holland kino likewise forms large, uneven, angular, blackish-brown fragments, with an astringent bitter taste. The Asiatic is likewise met with in irregular, brittle, blackish-brown fragments, which have little lustre and a pure astringent taste. African kino, on the contrary, is generally met with in small, angular, sharp-edged, glittering granules of a black colour; the thin splinters are ruby-red by transmitted light; it yields a beautiful brownish-red powder, and has a pure astringent taste. It is this last sort, which is the officinal kind, and the one most frequently met with in commerce, that the author has examined.

According to Vauquelin, African kino consists of 75 parts tannin and extractive, 24 parts mucilage and 1 part fibre. Berzelius examined the kino-tannin, which according to him is obtained in the following manner:—The kino is exhausted with water, the tan-

nin precipitated by sulphuric acid from the filtered solution, and the reddish-coloured precipitate washed with water until it shows no further reaction; the residue is then dissolved in boiling water, and so much barytic water added to the solution as is requisite to remove the sulphuric acid. After filtration, the solution is evaporated *in vacuo* over sulphuric acid, when a red, transparent, fissured mass, with a purely astringent taste, is obtained.

The author prepared the tannin according to the above method, employing carbonate of baryta to saturate the sulphuric acid; the products however did not possess a constant composition.

The astringent substances were dried in a water-bath at 212°, and burnt with oxide of copper and the addition of chlorate of potash. The following results were obtained from one preparation—

	I.	II.	III.
Carbon	44·63	44·85	44·69
Hydrogen	4·08	4·11	4·44
Oxygen	51·29	51·04	50·87

A second preparation according to the same method furnished a product which differed in its composition from the first. It gave—

	I.	II.	III.
Carbon	42·63	43·12	42·66
Hydrogen	3·62	3·68	3·68
Oxygen	53·75	53·20	53·72

This difference is owing to the energetic action of the sulphuric acid upon the kino substances, and the easy decomposability of the tannin in this mode of preparation. But it is moreover likewise probable that the tannin is modified during the slow washing and by boiling the precipitate with water. The author therefore endeavoured to procure the pure tannin in a different manner. The extract of kino obtained by rapid exhaustion with water, which was of a beautiful wine-red colour and had a very strong astringent taste, was mixed with a hot solution of isinglass, when a red, almost flesh-coloured bulky precipitate was produced; it was collected upon a filter, and boiled quickly in alcohol of 0·815 spec. grav. This beautiful red solution, which left a small portion of the tannin combined with the gelatine, was freed from alcohol by distillation, and evaporated under the air-pump over sulphuric acid to perfect dryness, when it furnished a red, shining, gummy mass of less specific gravity than kino-tannin, and with a pure and strongly astringent taste.

Submitted to analysis, it furnished the following results:—

	I.	II.	III.	IV.
Carbon	48·25	48·31	48·41	48·29
Hydrogen	4·37	4·29	4·21	4·27
Oxygen	47·38	47·40	47·38	47·44

Kino-tannin forms a red mass, which almost resembles metallic copper in colour and lustre when evaporated from a dilute solution in a porcelain dish. It is, as above stated, soluble in water, and still more so in alcohol, but is nearly insoluble in æther; the strongly astringent solutions have a somewhat acid reaction; it

yields no pyrogallic acid on dry distillation, and when heated in a glass tube is charred into a light cinder. The aqueous solution of the tannin is at first coloured of a deeper red by an aqueous solution of potash, and after a long interval an inconsiderable red precipitate is formed; when the aqueous solution is evaporated, it leaves a dark brown extractive mass; a moderately concentrated alcoholic solution of potash, added in drops to an alcoholic solution of tannin, causes the production of pale and dirty red flakes, which, collected on a watch-glass and exposed to a gentle heat, resemble groups of crystals.

Ammonia produces red streaks, and subsequently a small precipitate; the carbonated alkalies likewise produce inconsiderable pale red precipitates. Chromate of potash furnishes a brown precipitate passing into a yellowish-green, which, boiled for some time, acquires a greener colour, is insoluble in potash, but forms a beautiful red solution with hydrochloric acid, which however soon turns yellow.

When the aqueous solution is heated to boiling with a small excess of carbonate of magnesia, it forms a red compound inclining to violet; the filtered liquid has an intense rose colour, and contains not a trace of tannic acid. When this compound of tannate of magnesia is boiled with water or alcohol, not a trace is dissolved; when however the boiling is long continued, the compound acquires a more violet colour.

When the solution is mixed with acetate of lead, a reddish-gray insoluble compound is formed, the whole of the tannic acid is immediately appropriated, and the filtered liquid is scarcely coloured. This compound is wholly insoluble in boiling water, alcohol and potash; nitric acid however quickly dissolves it. It is very difficult to decompose by sulphuretted hydrogen, on which account the lead salt is not adapted to the preparation of the tannin.

Protosulphate of iron produces at first not the slightest opacity, but after a long time a grayish-green precipitate is formed. With persalts of iron it gives a blackish-green compound, which disappears somewhat on boiling in water. Nitrate of silver produces at first a faint red colouring, but the liquid is soon coloured grayish-black with reduction of silver. The protonitrate and perchloride of mercury give flesh-coloured precipitates. Sulphate of copper gives a gray precipitate, which after some time turns black. Tartar-emetic causes no precipitate.

Chlorine passed into the solution decolorizes it, and imparts to it a yellow colour. Cold nitric acid causes at first a turbidness, the liquid gradually becomes of a paler red, and after twelve to twenty-four hours it has a yellow colour. But when the dry tannin is mixed with nitric acid and heated to boiling, or a solution of the tannin poured into hot nitric acid, it is converted completely into oxalic acid. Sulphuric acid changes it into a dark blackish-brown mass. Hydrochloric acid renders the solution somewhat turbid at first, and after a time produces a pale red precipitate.

But the most remarkable change that this tannin experiences is when its *aqueous* solution is exposed for some length of time to the

air. When a filtered aqueous extract of kino is left for several weeks in broad open vessels, a sediment in the form of a bright red paste is seen to separate, which is further increased by heat; when kino is boiled in water, it separates in considerable quantity from the blood-red solution on cooling. But the same change is produced in the aqueous solution of pure kino-tannin by the access of air; it deposits a bright red substance, and the astringent taste has partially disappeared. The author observed the same in the decoction of the precipitate obtained by sulphuric acid. Hence it follows, that according to the method of preparation by sulphuric acid we are not certain of obtaining unaltered tannin. On the other hand, there is no fear of any change in a strong spirituous solution, for even after a tolerable portion of the alcohol had evaporated, the solution remained in an open vessel perfectly transparent, without sediment, and of a beautiful currant-red colour; nor was any change observed in an alcoholic solution which was quickly evaporated on the sand-bath.

Kino-Red.—That the change just described is produced by the action of the oxygen of the air is beyond doubt. When oxygen is passed at the ordinary temperature into an aqueous extract of kino, or even into a solution of the pure tannin, the solutions become very slightly turbid; but at a temperature of 68° to 86 F.°, after passing 2 cub. centims. oxygen into an extract of kino in about 3 to 4 oz. of liquid, it soon grew turbid, and deposited a copious bright red sediment; the same was the case with the solution of pure kino-tannin, a concentrated solution of which congealed to a light red paste, which had scarcely any astringent taste, for the tannin disappears with the change.

This bright red substance forms, when freed from all tannin, by washing upon the filter, a red amorphous mass with scarcely any taste; the author calls it *kino-red.* In composition it varies, especially that artificially prepared, according to the amount of oxygen absorbed. It shows however how much more oxygen the kino-red formed in solutions of kino-tannin by the access of air contains than kino-tannin itself. The material used for the following analyses was taken from an extract of kino which had been exposed three weeks to the air. The substance was dried slowly in the water-bath between 122° and 140° F., after having been previously dried on the filter in the air:—

	I.	II.
Carbon	37·69	37·41
Hydrogen	3·86	3·79
Oxygen	58·45	58·80

The composition of another sample which had been formed from a solution of pure kino-tannin by the access of air differed by some per cents., as follows:—

	I.	II.
Carbon	35·16	34·76
Hydrogen	3·90	4·02
Oxygen	60·94	61·22

On the other hand, the analyses which were made with kino-red by direct oxidation differed very considerably. Some furnished from 10 to 12 per cent. more oxygen than the above.

When this red substance is dried, it shrinks considerably, acquiring externally a brownish colour; it furnishes on trituration a beautiful bright red powder. A little pyro-acid is formed when it is strongly heated in a glass tube. In the dry state kino-red is sparingly or not at all soluble in water; in the hydrated state it is more soluble. It dissolves more readily in alcohol, but not at all in æther; the alcoholic solution has a feeble acid reaction.

Potash dissolves it with a dark red, ammonia with a dark violet colour, but it is again precipitated by acids. Solutions of baryta and chloride of calcium cause dark red flocculent precipitates in the ammoniacal solution. When heated with carbonate of potash, it is quickly dissolved with a beautiful dark red colour; it is converted into a blackish-brown mass by concentrated sulphuric acid. Nitric acid converts kino-red completely into oxalic acid; chlorine decolorizes it; acetic and tartaric acids dissolve it with a dark red colour.

Kino-Brown.—Most interesting is the change which hydrochloric acid produces. When kino-red is boiled with strong acid, it dissolves after some time with a beautiful intense violet colour; and on cooling, and especially on dilution with water, deposits a splendid dark brown powder, which held against the light has a shade of lilac, whilst the supernatant liquid has a dark rose colour. When the mass is brought upon a filter, and washed to free it from hydrochloric acid, it colours the filter deep rose-red. This colouring substance the author has called *kino-brown*. It dissolves in from 20 to 30 parts of strong spirit, with a red colour inclining to violet, and has a neutral reaction. It dissolves in acetic acid when warm, with a poppy-red colour; it is equally soluble in tartaric acid. As this beautiful substance may probably prove useful to the dyer, it was submitted to analysis. After having been dried at 212°, it furnished—

	I.	II.
Carbon	44·77	45·05
Hydrogen	4·39	4·19
Oxygen	50·84	50·76

In case this pigment should be used for dyeing, the simplest method of preparing it would be to boil the pulverized kino for some time with water, to collect upon a filter the substance which separates in abundance on the cooling of the concentrated solution, to convey it into hydrochloric acid, and proceed as above directed. In this manner a beautiful kino-brown is obtained.

A solution of kino-brown in acetic acid or spirit communicated a pale rose colour to stuffs prepared with iron mordants. It dyed wool and cotton moderately well, linen better, and silk best of all.

Alum mordants do not appear well-suited, for all the stuffs dyed with it, excepting silk, acquired a dirty red colour, the latter a brown-red.

Tin mordants appear to be best adapted for this pigment. Stuffs,

especially silk, are coloured by solutions in alcohol, still better in acetic acid, of a beautiful red, shading from rose-red into poppy-red.

Silk is dyed of a most beautiful intense rose-red inclining to lilac by kino-brown and tin mordants when a very dilute solution in hydrochloric acid is employed. This acid however is far more injurious to the stuffs than the other weaker acids.—*Archiv der Pharm.*, lxv. p. 283.

On the Colouring Matters of Fustic (Morus tinctoria). *By* Dr. R. Wagner.

[Continued from page 245.]

Action of Concentrated Sulphuric Acid upon Moritannic Acid.—When finely powdered moritannic acid is triturated with sulphuric acid, a brownish yellow solution is obtained, from which, after some time, a brick-red amorphous mass separates, which has the property of yielding a magnificent carmine solution on being mixed with the smallest quantity of ammonia or potash. On account of this property, the author calls this substance *rufimoric acid*. It is highly interesting from its very probably being perfectly identical with carminic acid.

In order to obtain it in a pure state and to free it from adherent sulphuric acid, the mass is collected upon a filter, and washed with cold water until what passes through has only a feeble acid reaction; it is then dissolved in the smallest quantity of boiling alcohol, the solution filtered, and after having removed the greater portion of the alcohol by evaporation on the water-bath, it is poured into 50 times the quantity of cold water, constantly stirring. A bulky, flocculent red precipitate falls, which is collected upon a filter, washed with cold water, pressed between blotting-paper, and dried at a low temperature.

Another method of obtaining this substance in a state of purity, which is somewhat more tedious, but entails no loss, consists in diluting with water the red liquid produced by the digestion of the moritannic acid with sulphuric acid, neutralizing the liquid accurately with carbonate of soda, adding a few drops of acetic acid, and precipitating the rufimoric acid by a boiling solution of neutral acetate of copper. The bulky reddish-brown precipitate, consisting of rufimorate of copper, is suspended in water and decomposed with sulphuretted hydrogen; the eliminated rufimoric acid is partly held in solution, but the greater portion adheres to the sulphuret of copper, from which it is separated by treatment with boiling alcohol. The alcoholic solution, upon evaporation in the water-bath, leaves a greenish-red mass.

The rufimoric acid prepared according to the above method forms when dry a dark red mass, which exhibits in a state of fine division a beautiful red colour. It dissolves readily in alcohol, far less in water, and very sparingly in æther; the smallest addition of ammonia renders the acid soluble in every proportion in water. The solutions have a weak acid reaction. Rufimoric acid dissolves in

concentrated sulphuric acid with a red colour. From the solution it is partly precipitated by water. It dissolves in hydrochloric acid without decomposition. Caustic and carbonated alkalies give carmine-red solutions, which remain for a long time unaltered in the air, and lose their red colour very slowly.

Rufimoric acid may be heated to 266° F. without alteration, but above that temperature it gives off fumes, which condense in part. The condensed crystalline mass is colourless, and behaves towards reagents like phenic acid. The behaviour of rufimoric acid towards reagents is as follows:—An aqueous solution, to which a trace of ammonia had been added, was employed for the experiments. A solution of alum gave no precipitate; on the addition of ammonia, a dark red lake was formed; protochloride of tin and chloride of barium behaved in the same manner; neutral acetate of lead gave a dark red, acetate of copper a brownish-red flocculent precipitate. Sulphate of tin and nitrate of silver caused no precipitate. Nitrate of lead gave a cherry-red, protonitrate of mercury a brownish-red, pernitrate of mercury a reddish precipitate. Perchloride of iron causes a dark brown colour, but no precipitate. An alcoholic solution of rufimoric acid is precipitated by an alcoholic solution of potash; the precipitate is dark red and tenacious. Chlorine destroys the solution of rufimoric acid, with elimination of brown flakes.

Nitric acid furnishes, on being heated with rufimoric acid, a yellow solution, from which a large quantity of oxalic acid and crystals of a nitro-acid are deposited, which differ from nitrophenissic acid by their deportment towards baryta and the protosulphate of iron.

When rufimoric acid is boiled with a solution of caustic potash or barytic water, the carmine-red solution soon acquires a dark yellow colour, and then contains no more rufimoric acid. When the solution is neutralized with acetic acid, perchloride of iron produces a blackish-green precipitate, which is characteristic of moritannic acid; the solution precipitates gelatine, and is coloured blood-red by ammoniacal tartrate of iron. Rufimoric acid has therefore again passed into moritannic acid, if we admit that it was produced from moritannic acid merely by the loss of water. The latter however is partially decomposed by the combined action of the alkalies and a high temperature; for when such a solution, which has been kept boiling for some time, is supersaturated with dilute sulphuric acid, a brown humus-like mass separates; the filtered liquid is colourless, is coloured yellow by alkalies; and behaves like a solution of moritannic acid. On analysis, rufimoric acid furnished—

Carbon.....	54·83	54·34	54·23	14	= 84	54·19
Hydrogen....	4·31	4·38	4·70	7	7	4·52
Oxygen.....	..	..	..	8	64	41·29

Rufimorate of Lead, $C^{14}H^{7}O^{8}$, 2PbO.—Rufimoric acid was dissolved in alcohol, and then precipitated with an alcoholic solution of neutral acetate of lead; the precipitate was washed with alcohol, and dried at 212°. The lead salt forms a dark scarlet-red crystalline powder, insoluble in water and in alcohol, but soluble in acetic

acid with a yellowish-red colour. In potash it dissolves with a carmine-red colour; with ammonia it furnishes a yellowish-green precipitate, the liquid filtered from which is colourless.

To prepare the copper salt, the solution of the rufimoric acid was precipitated by a solution of neutral acetate of copper, and the reddish-brown precipitate washed by decantation. When dried, it furnished a dark reddish brown mass, which gave a dark red powder, and contained 27·1–27·7 per cent. oxide of copper. On comparing the properties and the composition of rufimoric acid with those of the carminic acid discovered by Warren de la Rue, the two substances appear to be identical. The formula of the copper salt decided De la Rue to give the formula $C^{28}\ H^{14}\ O^{16}$ to his acid, which furnished on elementary analysis—

Carbon	54·13
Hydrogen	4·62
Oxygen	41·25

It must be admitted that if rufimoric and carminic acid are identical, this acid is capable of combining with oxide of copper in several proportions. The author could not succeed in obtaining a salt of the formula $2C^{14}\ H^{7}\ O^{5}$, CuO. De la Rue states that carminic acid dissolves in water in every proportion, but not in æther. Rufimoric acid is likewise soluble in water when the merest trace of ammonia has been added to it. De la Rue found the greatest difficulty in obtaining carminic acid free from nitrogen; an exceedingly minute quantity of ammonia may therefore have given rise to the greater solubility in water. With respect to the insolubility in æther, the author found that rufimoric acid containing a trace of ammonia was very difficult of solution in æther. Carminic acid does not appear to be absolutely insoluble, as it is not precipitated by æther from an alcoholic solution.

On the Products of Decomposition of Morine.—Morine and moritannic acid constitute the yellow pigments of fustic. Chevreul, who first examined the colouring substances of this wood, states that the morine can be partially sublimed unaltered. The author has proved that Chevreul did not experiment with pure substances, and that he regarded morine-lime as the pure pigment. When morine is heated in a metallic bath, it is scarcely altered at 482°, but at 572° it turns black, disengages a large quantity of carbonic acid, whilst a small quantity of a yellow oil distils over, which condenses in the receiver into crystalline granules; moreover there is formed a tolerable quantity of phenylous acid. The crystalline sublimate behaves towards reagents exactly like phenic acid.

Since morine furnishes, when heated, the same product as moritannic acid, it may be viewed as the gallic acid of the latter; the pyro-acid stands consequently in the same relation to both as pyrogallic to tannic and gallic acids; the isomerism of the two substances is in favour of this view, but opposed to it is the circumstance that hitherto it has not been possible to convert the moritannic acid into morine. The identity of the products of decomposition of

morine and of moritannic acid has been proved by the complete agreement of all the reactions, but not by elementary analysis.

Behaviour of Morine towards Concentrated Sulphuric Acid.—When finely-powdered morine is treated with concentrated sulphuric acid, a dark yellowish-brown solution is obtained, from which no red substance separates either on the application of heat or long standing. Morine is precipitated unaltered from the solution by water. When the sulphuric solution is heated, it is decomposed with disengagement of sulphurous and phenylous acids.

A remarkable difference therefore occurs in the behaviour of morine and moritannic acid towards sulphuric acid. Whilst moritannic acid is converted into rufimoric acid by concentrated sulphuric acid, morine remains unaltered under the same circumstances. This is the reverse of what takes place with quercitannic acid, which is not converted by sulphuric acid into a red acid, whilst gallic acid is easily metamorphosed into a red substance. From this investigation the author deduces the following conclusions:—1. Moritannic acid and morine yield on dry distillation a crystalline acid, possessing the formula $C^{12} H^6 O^4$, to which has been assigned the name phenic acid (pyromoritannic acid), and which appears to be identical with the pyrocatechine of Zwenger. 2. Moritannic acid furnishes, on treatment with concentrated sulphuric acid, a red acid, $C^{14} H^7 O^8$, which has been called rufimoric acid, and possesses the same composition and properties as the carminic acid discovered by De la Rue.—*Journ. für Prakt. Chem.*, lii. p. 450.

On the Explosive Compound usually denominated Iodide of Nitrogen.

By J. H. Gladstone, Ph.D., F.C.S.*

The following experiments were made last summer with a view to settle the real composition of the so-called "iodide of nitrogen." This substance, resulting from the mutual action of iodine and ammonia in solution, has already been the subject of much investigation; and the study of its reactions by different chemists has led to four different formulæ being assigned to it. The extremely explosive character of the substance precludes the idea of analysing it in the usual manner, as it would be impossible to place a portion in the scale-pan of a balance with any safety after it had been dried. Indirect modes of analysis, by which the relative proportion of its constituent elements is determined, appear to be offered by various decompositions, which the black powder may be made to undergo. M. Bineau† alone has studied any of these hitherto; and his experiments led him to assign to the so-called iodide of nitrogen the composition NHI^2. The quantitative results recorded below attest the truth of this formula.

The substance employed by me was always prepared by decomposing an alcoholic solution of iodine by means of ammonia in excess. The black powder thus formed was completely washed by

* Communicated by the Author, having been read before the Chemical Society.

† Ann. Ch. Phys. [3] xv. 71.

suffusion with distilled water and decantation. It was found that during this reaction an amount of iodide of ammonium is formed slightly exceeding half the amount of iodine employed; a mere trace of iodic acid is also produced. This fact is opposed to the formula NI, assigned to the black powder by Mitscherlich, for

$$4NH^3+4I=NI+3NH^4I,$$

in which case the iodide of ammonium obtained would be quite three-fourths of the iodine originally acted upon; but it decides nothing as to whether 1, 2 or 3 atoms of hydrogen in the ammonia are substituted by iodine, for

$$2I+2NH^3= NH^4I+NH^2I \quad \text{(Millon).}$$
$$4I+3NH^3=2NH^4I+NHI^2 \quad \text{(Bineau).}$$
$$6I+4NH^3=3NH^4I+NI^3.$$

The black powder suffers spontaneous decomposition in pure water. Bubbles of gas are slowly given off, iodine is set free, and the solution (which is acid to test-paper) contains hydriodic and iodic acids, together with ammonia. In an attempt to make use of this decomposition as a means of analysis, the iodic acid was found to be to the hydriodic acid in the ratio of 1 atom to 8·44 atoms; but it is not likely that the two acids always maintain the same proportion.

The addition of ammonia to the water in which the black powder is immersed tends to prevent its spontaneous decomposition. Potash, on the contrary, accelerates it. So do acids in general. A solution of carbonate of potash has much the same action as pure water.

Chlorine destroys the black powder, but not instantaneously; bromine water causes its immediate decomposition; strong nitric acid attacks it violently.

Hydrosulphuric acid causes its instant decomposition without the evolution of any gas, and with the formation of ammonia and hydriodic acid alone, sulphur being in the meantime deposited. This affords a ready method of determining the relative proportion of iodine and nitrogen. Accordingly some of the black powder was diffused through water, and a stream of hydrosulphuric acid gas was passed through it until the solution, which assumed at first a red tint, became colourless, and smelt strongly of the gas. It was then gently heated and filtered, the hydriodic acid was precipitated as silver salt, excess of silver was removed by the addition of a large excess of hydrochloric acid, and the resulting chloride of ammonium was estimated in the usual manner. The amount of ammoniochloride of platinum obtained was 5·83 grs., that of iodide of silver 12·53 grs., which is equivalent to

Nitrogen	0·366 grs.
Iodine	6·75 ...

If we divide these numbers by the atomic weights of the respective elements, we obtain—

Nitrogen	261
Iodine	533

or the proportion of 1 atom of nitrogen to 2·04 atoms of iodine.

The action of sulphurous acid appeared to offer the means of determining the relative proportion of nitrogen, iodine and hydrogen also, if that element really be a constituent of the black powder. The transformation of the substance into ammonia and hydriodic acid takes place instantly, without the evolution of any gas, unless the temperature be suffered to rise considerably, when a secondary action is instituted. At the same time, a quantity of sulphurous acid is converted into sulphuric acid, equivalent of course to the quantity of water decomposed, in order to supply the necessary hydrogen. A carefully-prepared fresh solution of sulphurous acid was added gradually to some of the black powder diffused through water, until the decomposition was complete. The solution thus obtained was divided into two equal portions. The one portion was evaporated down with excess of hydrochloric acid, and the ammonia was converted into platinum salt; the other portion was very gently warmed to expel sulphurous acid; nitrate of silver was added to precipitate the iodine, and subsequently the sulphuric acid was thrown down as baryta salt. There were obtained 8·65 grs. of ammoniochloride of platinum, 18·53 grs. of iodide of silver and 17·57 grs. of sulphate of baryta. This is equivalent to—

Nitrogen	0·542 grs.
Iodine	9·98 ...
Sulphuric acid	6·04 ...

Dividing these numbers by the atomic weights, we obtain—

Nitrogen	388	or	1 equiv.
Iodine	788	or	2·03 equivs.
Sulphuric acid	1520	or	3·92 equivs.

This confirms the preceding result, and shows moreover that the black powder contains 1 equiv. of hydrogen; for 1 atom of ammonia, 2 atoms of iodine and 4 atoms of sulphuric acid can only arise from 4 atoms of sulphurous acid, 4 atoms of water and NHI^2—

$$NHI^2+4SO^2+4HO=NH^3+2HI+4SO^3.$$

Serullas* observed, that when this black powder is decomposed by dilute hydrochloric acid, a red solution is obtained, from which the addition of an alkali reprecipitates the explosive compound, a portion however being always decomposed into its elements. Millon† made the further observation, that if the black powder be treated with a saturated solution of hydrochloric acid, it disappears without the evolution of any gas, and the resulting solution is neutral to test-paper. He believes that the substance is resolved into ammonia and the acids of iodine, and concludes from this peculiar reaction that the explosive body must have the composition NH^2I. It is difficult to see how this conclusion follows from the premises; the

* Ann. Ch. Phys. xlii. p. 200. † *Ibid.*, [2] lxix. p. 88.

more natural idea would be, that the black powder, being ammonia in which a portion of the hydrogen is replaced by iodine, combines as such with the hydrochloric acid, thereby neutralizing it. Yet Serullas has long since recorded various reasons tending to prove that this is not the case. He believed that the solution contained iodic and hydriodic acids, along with the hydrochloric acid; and what confirmed him in this belief was the observation, that when these two acids of iodine are mixed together and supersaturated with ammonia, the explosive compound is obtained, especially if hydrochloric acid be present. Now this certainly arises from the two acids, when mixed, reacting upon one another to produce free iodine; and the explanation of the eminent chemist just mentioned does not account for the fact, that when the decomposition of the black powder has been effected by water, or other acids than the hydrochloric, a solution is obtained, from which ammonia does not reprecipitate it.

On repeating the experiment, I found that the red solution obtained by dissolving the explosive compound in strong hydrochloric acid contains not a trace of free iodine; it gives no blue colour with starch. When evaporated to dryness in a water-bath, it comes out as a solid body of a somewhat yellow colour, soluble in water or alcohol, and neutral, or nearly so, to test-paper. If potash or baryta water be added to this solution, it reprecipitates the black powder. The addition of nitrate of silver causes a mixed precipitate of chloride and iodide of silver. Sulphurous acid gives rise to a separation of iodine, which a larger quantity converts into hydriodic acid. The dried substance, when heated *per se*, suffers decomposition; it gives off a pungent odour, then iodine sublimes, and afterwards chloride of ammonium. Æther extracts from the evaporated solution that which imparts to it its colour, and leaves some chloride of ammonium behind. All these reactions are perfectly explained by considering the solution produced by means of hydrochloric acid as a mixture of chloride of ammonium and protochloride of iodine. The reaction is as follows:—

$$NHI^2+3HCl=NH^4Cl+2ICl.$$

And it has been already ascertained by Mitscherlich that the explosive compound is produced when protochloride of iodine is treated with ammonia. The reaction in this case will be—

$$2ICl+3NH^3=NHI^2+2NH^4Cl.$$

The same chemist states that terchloride of iodine with ammonia causes the formation of the same black powder. If this be really the case, we must suppose that some one of the oxygen compounds of chlorine is formed at the same time. But an aqueous solution of terchloride of iodine is, to say the least, of very uncertain constitution; and even the liquid resulting from the action of *aqua regia* upon iodine may contain the protochloride. If iodic acid be dissolved by strong hydrochloric acid in the cold, a yellow solution is obtained having a chlorous odour; but I find that the addition of ammonia causes no black precipitate in such a solution, unless it has been previously heated.

In accordance with the practice now adopted in naming those compounds in which 2 equivs. of hydrogen in ammonia are replaced by 2 of another body, this explosive compound should bear the appellation "Iodimide."

When this paper was read before the Society, Dr. Playfair remarked, that some time since he had prepared the same explosive powder by pouring a solution of hypochlorite of lime into a solution of iodide of ammonium. He believed they were in the proportion of single equivalents; and as this reaction may be readily explained under the supposition that the compound is $NH^2 I$, it had confirmed in his mind the view propounded by Millon. Upon considering the reaction subsequently, I perceived that a compound, having Bineau's formula, might equally be obtained from the same salts in the same proportions, but that ammonia would appear among the products of decomposition. The reaction might be either

$$CaO, ClO + NH^3 I = NH^2 I + CaCl + 2HO$$

or $$2(CaO, ClO) + 2NH^4 I = NH\,I^2 + 2CaCl + 4HO + NH^3.$$

Upon repeating the experiment with bleaching powder, any alkaline reaction of which had been more than neutralized by acetic acid, I found a large quantity of ammonia set free. This reaction then, like every other with which I am acquainted, indicates the same composition for this explosive powder, namely NHI^2.

On the Production of Lactic Acid in the Fermentation of Malate of Lime. *By* E. J. Kohl.

The author obtained lactate of lime in the fermentation of caseine with malate of lime procured from the nearly-ripe berries of the mountain ash, in order to prepare succinic acid. 8 lbs. of malate of lime, 30 to 35 lbs. of distilled water, and caseine which had not attained the highest degree of putrefaction, were allowed to act on each other at 64° to 82° F. In eighteen days the fermentation, during which carbonic acid was disengaged, was complete.—*Archiv der Pharm.*, lxv. p. 17.

On Istrian Gall-Nuts. *By* M. Roder.

The author finds that these galls, which have been of late highly recommended, contain only 24 per cent. of tannin, and are therefore much inferior to the Aleppo gall-nuts, which contain three times the quantity.—*Central Blatt.*, May 28, 1851.

On the Compound Ammonias. *By* A. Wurtz.

[Concluded from page 255.]

Amylamine, $C^{10} H^{13} N$.—This base is formed by the action of potash upon the amylocyanic and amylocyanuric æthers. It is iso-

lated by decomposing the muriate with lime in a retort. In order to obtain it anhydrous, it is rectified over potash or baryta.

Pure amylamine is a very light, mobile, perfectly-colourless liquid; its odour resembles at the same time that of ammonia and the amylic compounds; it is exceedingly caustic. Its specific gravity at 18° C. is 0·7503; it boils at 95°; it burns with a luminous flame, which is pale at the margins and towards the end; it absorbs carbonic acid from the atmosphere, and is converted into carbonate; it mixes in every proportion with water, and precipitates nearly all metallic oxides from their solutions, as follows:—

Salts of	Colour of precipitate.	In an excess.
Magnesia,	white,	insoluble.
Alumina,	white, flocculent,	soluble.
Oxide of chromium,	green,	insoluble.
Peroxide of iron,	yellowish-brown,	insoluble.
Oxide of uranium,	yellow, flocculent,	insoluble.
Nickel,	apple-green,	insoluble.
Cobalt,		insoluble.
Zinc,	white, gelatinous,	insoluble.
Manganese,	white, becoming brown,	insoluble.
Copper,	bluish-white,	soluble.
Silver,	light brown, flocculent,	sol. in large excess.
Protonitrate of mercury,	blackish-brown,	insoluble.
Perchloride of mercury,	white,	insoluble.
Acetate of lead,	no precipitate.	
Nitrate of lead,	white,	insoluble.
Cadmium,	white,	insoluble.
Bismuth,	white,	insoluble.
Protochloride of tin,	white,	insoluble.
Antimony,	white,	insoluble.
Gold,	yellowish-brown,	sol. in large excess.
Platinum,	pale yellow, crystalline,	soluble in water.

Analysis of amylamine:—

Carbon	68·52	10 =	60	68·96
Hydrogen	15·03	13	13	14·94
Nitrogen	..	1	14	16·10

Hydrochlorate of Amylamine, $C^{10}H^{13}N$, HCl.—The product of the distillation of the cyanate of potash with sulphamylate of potash is distilled with a concentrated solution of potash. The amylocyanic æther, and the amylocyanuric æther contained in it, are decomposed into carbonate of potash and amylamine. The decomposition of the amylocyanuric æther is most difficult, and is complete only when the whole of the water is distilled off and the potash is in the state of fused hydrate. The liquid distillate sometimes separates into two layers; it is saturated with hydrochloric acid, and the salt obtained by recrystallization in white scales, which are fatty to the touch and dissolve in alcohol and water. They do not deliquesce in the air. They furnished on analysis—

Carbon	48·30	10 =	60·0	48·58
Hydrogen.....	11·48	14	14·0	11·33
Chlorine	28·32	1	35·5	28·73
Nitrogen	..	1	14·0	11·36

Hydrochlorate of Amylamine and Platinum, $PtCl^2$, $C^{10}H^{13}N$, HCl, is formed on mixing a solution of bichloride of platinum with hydrochlorate of amylamine. It is rather soluble in water, on which account alcohol is added to the mixture. The precipitate is dissolved in boiling water, whence the double salt crystallizes in beautiful golden spangles, which furnished on analysis—

Carbon.....	20·47	10 =	60·0	20·47
Hydrogen	4·85	14	14·0	4·77
Nitrogen	..	1	14·0	4·77
Chlorine	35·88	3	106·5	36·33
Platinum.....	..	1	98·6	33·66

Hydrobromate of Amylamine.—It was obtained in the action of bromine upon amylamine, and with this salt is simultaneously produced a brominated product of substitution.

This salt itself is not deliquescent, melts at a slightly-elevated temperature, giving off white inflammable vapour. It is very readily soluble in water and alcohol, sparingly soluble in æther, by which it is precipitated from an alcoholic solution in nacreous scales.

Amyloxamide is formed on mixing amylamine with oxalic æther in very slender silky needles, which melt at 139° C. At a higher temperature it escapes in white vapour, leaving no residue. Amyloxamide is insoluble in water, but soluble in alcohol, from which it again separates almost entirely on cooling.

The three bases, ammonia, methylamine and æthylamine, can be separated in the following manner:—The mixture is saturated with hydrochloric acid. From the perfectly-dry mixture, absolute alcohol removes only the hydrochlorates of methylamine and æthylamine, leaving untouched the chloride of ammonium. The two hydrochlorates are then converted into sulphates, and the dry salts treated with absolute alcohol. The sulphate of æthylamine dissolves, whilst the sulphate of methylamine remains undissolved.

Constitution of the Ammonia Bases.—It may be assumed that the hydrocarbon C^4H^4, if we ascribe to it the power of uniting with water to form æther, may likewise combine directly with ammonia to furnish a base. In accordance with this supposition, these bases would have the general formula C^nH^n, NH^3, and they would range with the conjugate compounds. Wurtz enumerates some further relations which tend to favour this view, but finally declares for the opinion, that these bases are produced from ammonia by substitution; 1 equiv. hydrogen is eliminated from the ammonia, and its place taken by the radical of the alcohols of the general formula C^nH^{n+1}. The author is led to this principally by the three following reasons:—

1. The ammonia bases, as shown by Hofmann, are formed in the action of hydrobromic æthers upon ammonia. In this case the bro-

mine, owing to its great affinity for hydrogen, combines with it; the eliminated equivalent of hydrogen is replaced by the alcohol radical, and so the new base formed, which immediately combines with the hydrobromic acid, for instance $C^4 H^5 Br$ (bromide of æthyle, hydrobromic æther) $+ NH^3 = HBr + C^4 H^7 N$.

2. The ammonia bases form no nitryles. Hofmann found that aniline is an ammonia base analogous to æthylamine, and that anhydrous phosphoric acid did not remove 4 equivs. water from it in order to convert it into nitryle, but caused further decomposition. Hofmann therefore concluded that there could no longer be any ammonia contained in it, but that 1 equiv. hydrogen was already replaced by an alcohol radical, owing to which substitution, the salt submitted to the action of the anhydrous phosphoric acid no longer contained the 4 equivs. of hydrogen existing in NH^3, HO, requisite for the formation of 4 atoms of water. The experiments above detailed, on the action of anhydrous phosphoric acid upon acetate of æthylamine, æthylacetamide, æthyloxamide, and methyloxamide, which are carbonized by it, support this view; but the author confesses that this conclusion may be deceptive, owing to the easy decomposability of the substances.

3. A reason is found, from the following consideration, that the alcohol radicals exist in the ammonia bases. Furfurole, $C^{30} H^{12} O^{12}$, combines with 2 equivs. ammonia $= N^2 H^6$; 6 equivs. water separate, and the substance produced is furfuramide, $C^{30} H^{12} N^2 O^6$. Now if this has been produced, as we may assume to be the case, by the actual reduction of the 6 equivs. of hydrogen in the $N^2 H^6$ by the 6O of the furfurole, then we may presume that with æthylamine, 2 equivs. of which contain no longer 6, but only 4 equivs. of the original basic hydrogen of the ammonia, no compound corresponding to furfuramide ought to be produced; now such, in fact, is the case. It does not act upon furfurole in the cold, and when heated, black resinous products of decomposition are obtained; and so it ought to be if the ammoniacal bases contain alcoholic groups substituted for hydrogen, for in the present case 2 equivs. æthylamine

$$\begin{matrix} & H & & & H & \\ N & & H & + N & & H \\ & C^4 H^5 & & & C^4 H^5, & \end{matrix}$$

which contain altogether but 4 equivs. of basic hydrogen, are no longer capable, when acting upon furfurole, of producing 6 molecules of water.

Whatever hypothesis be adopted as to the constitution of the ammoniacal bases, I think it may be admitted without hesitation that they are homologous with each other and with ammonia. Each member differs from the other by $C^2 H^2$, and they all exhibit the most perfect analogy in their compounds. The series of bases $C^n H^{n+3} N$ is evidently quite as well characterized as the series of acids $C^n H^n O^4$. The individual members of this basic series are formed, starting from ammonia NH^3, by replacing successively a molecule of hydrogen by a term of the ascending series, $C^n H^{n+1}$.

There still remains the question to be answered, whether all the homologous series are formed in the same manner; whether, for instance, the series of the fatty acids $C^n H^n O^4$ is formed by the substitution of a term $C^n H^{n+1}$ for 1 equiv. of hydrogen, as long since asserted by Kolbe with respect to the fatty acids with 4 equivs. of oxygen. This distinguished chemist admits that the acids contain a molecule of oxalic acid intimately united with a term $C^n H^{n+1}$. The following will give a clear idea of M. Kolbe's hypothesis:—

$C^2 H^2 O^4 = C^2 O^3$, H, HO = formic acid.
$C^4 H^4 O^4 = C^2 O^3$, $C^2 H^3$, HO = acetic acid.
$C^6 H^6 O^4 = C^2 O^3$, $C^4 H^5$, HO = metacetonic acid.

If it be objected to Kolbe's view, that oxalic acid is bibasic, as asserted by Gerhardt, this might easily be met by stating it in a slightly different form. It may be admitted that all the fat acids derive from formic acid CHO^3, HO by the substitution of a term $C^n H^{n+1}$ for the equivalent of hydrogen not capable of being replaced by a metal, and forming part of the molecule of the acid itself. Kolbe's view deserves serious attention, for it is supported by many facts, for instance,—1st, the separation of the groups $C^n H^{n+1}$, or the polymeric members $2C^n H^{n+1}$, in the electrolysis of the volatile acids with 4 equivs. of oxygen; 2nd, the formation of nitryles by the action of anhydrous phosphoric acid upon the ammoniacal salts of these acids, for the nitryles or the cyanic æthers contain precisely the group $C^n H^{n+1}$ which theory indicates in the acid from which they are derived; 3rd, the decomposition of these same nitryles, under the influence of potash, according to the following equation:—

$$C^2 N, C^n H^{n+1} + H^3 O^3 + HO = C^2 O^3, C^n H^{n+1} HO + NH^3.$$

Hence the probability that—

1. The volatile acids $C^n H^n O^4$ are formed by the substitution in formic acid of $C^n H^{n+1}$ for 1 equiv. H.

2. The ammonia bases are also formed by the substitution in ammonia of $C^n H^{n+1}$ for 1 equiv. H.

The proposition may probably be reversed, and still remain true, that the homologous compound of an organic substance is produced when 1 equiv. hydrogen belonging to its molecule is replaced by $C^n H^{n+1}$. When this hydrogen belongs to the basic water of the substance, an æther or a vinic acid is obtained.

Constitution of the Alkaloids.—The facts detailed in this memoir allow of our drawing a conclusion as to the constitution of one division of the organic bases. Berzelius supposed that this class of substances contained ammonia conjoined with an organic group. Liebig admitted that the ammonia did not pre-exist in them, but was present in the form of an amidogen compound coupled with an organic group.

According to our author, the organic bases which contain no oxygen are true ammonias, ammonia in which a hydrocarbon is substituted for hydrogen, as follows:—

Ammonia..... $N\ H^3 = N\begin{matrix}H^2\\H\end{matrix} = NH^3$.

Methylamine ..... $N\ C^2\ H^5 = N\begin{matrix}H^2\\C^2\ H^3\end{matrix} = NH^3\ (C^2\ H^3)$.

Æthylamine ..... $N\ C^4\ H^7 = N\begin{matrix}H^2\\C^4\ H^5\end{matrix} = NH^3\ (C^4\ H^4)$.

(Propylamine)

Butylamine (petinine) $N\ C^8\ H^{11} = N\begin{matrix}H^2\\C^8\ H^9\end{matrix} = NH^3\ (C^8\ H^8)$.

Amylamine ..... $N\ C^{10}\ H^{13} = N\begin{matrix}H^2\\C^{10}\ H^{11}\end{matrix} = NH^3\ (C^{10}\ H^{10})$.

Nicotine ..... $N\ C^{10}\ H^7 = N\begin{matrix}H^2\\C^{10}\ H^5\end{matrix} = NH^3\ (C^{10}\ H^4)$.

Aniline ..... $N\ C^{12}\ H^7 = N\begin{matrix}H^2\\C^{12}\ H^5\end{matrix} = NH^3\ (C^{12}\ H^4)$.

Picoline ..... $N\ C^{12}\ H^7 = N\begin{matrix}H^2\\C^{12}\ H^5\end{matrix} = NH^3\ (C^{12}\ H^5)$.

Toluidine ..... $N\ C^{14}\ H^9 = N\begin{matrix}H^2\\C^{14}\ H^7\end{matrix} = NH^3\ (C^{14}\ H^6)$.

Coniine ..... $N\ C^{16}\ H^{15} = N\begin{matrix}H^2\\C^{16}\ H^{13}\end{matrix} = NH^3\ (C^{16}\ H^{12})$.

Cumidine ..... $N\ C^{18}\ H^{13} = N\begin{matrix}H^2\\C^{18}\ H^{11}\end{matrix} = NH^3\ (C^{18}\ H^{10})$.

Leucole ..... $N\ C^{18}\ H^7 = N\begin{matrix}H^2\\C^{18}\ H^5\end{matrix} = NH^3\ (C^{18}\ H^4)$.

Several of the oxygenated bases have evidently a similar constitution, for instance the ureas; their general formula is—

$$2\begin{pmatrix}H\\N\ H\\CO\end{pmatrix},$$

in which one or several equivalents of hydrogen are replaced by the term $C^n\ H^{n+1}$, as will be shown in a subsequent memoir.—*Ann. de Chim. et de Phys.*, xxx. p. 443.

On some Compounds of the Metallic Carbonates with the Carbonates of Potash, Soda and Ammonia. *By* H. St. Claire Deville.

A large number of reagents are employed in chemical analysis, with which the precipitation of metallic substances is effected only on the condition that certain precautions are attended to. Thus in general it is impossible to precipitate the metals by the alkaline carbonates, except by avoiding a large excess of the reagent, and boiling the mixture for some length of time. This fact, which is still imperfectly known, since we find it stated in all works on chemistry that the majority of the metallic carbonates are insoluble in an excess of carbonated alkalies, deserves special attention on account of its numerous applications in analysis and the errors it may

prevent from being committed. In fact very few of the metallic carbonates resist the solvent action of the alkaline carbonates; indeed double compounds may be obtained, resulting from the mutual reaction of these two classes of salts. These well-characterized compounds exhibit very beautiful crystalline forms, and frequently remarkable colours.

I have examined under this point of view the reactions of nearly all the metals,—iron, zinc, copper, cobalt, nickel, chrome, &c. All their carbonates have the property of forming, in various proportions, compounds with the carbonates of soda and potash. I shall here merely indicate the general results and my method of proceeding.

The neutral carbonates, the sesquicarbonates and the bicarbonates of soda and potash, do not act in the same manner on metallic solutions. The two last kinds of carbonates furnish double salts which differ from each other. Moreover, the carbonates of soda and potash, which have so striking an analogy in almost all cases, do not always furnish corresponding compounds with the same metals. The salts of copper furnish an example. If carbonate of copper be conveyed into a mixture of the two alkaline salts, the soda will be precipitated entirely, or nearly so, in the form of very brilliant crystals of a double carbonate, whilst the whole of the potash will remain in solution. Hitherto I have not been able to produce with potash a crystallized compound analogous to this carbonate of copper and soda. The same occurs with other metals.

The method which I adopt consists in pouring the metallic salt slowly into a concentrated solution of alkaline carbonate, and constantly agitating the liquid. In general a portion of the precipitate redissolves, but the other portion is converted into a mass of more or less bulky crystals, and the liquid gradually deposits the metallic substance which it contained. It thus appears that the double carbonate, as soon as it is formed, becomes insoluble in the alkaline carbonate, at the expense of which it was produced.

The carbonates of ammonia furnish with the carbonates of certain metals compounds, some of which have been examined by M. Favre. I have succeeded in forming with other metals, and in particular with nickel and cobalt and the various carbonates of ammonia, compounds in which the ammonia appears to act the same part as soda and potash. The double carbonates of ammonia and cobalt or nickel are easily formed by mixing the nitrates of these metals with an excess of bicarbonate of ammonia in closed vessels*. A salt is then obtained in micaceous plates, which corresponds in composition to the salt obtained under the same circumstances with the bicarbonate of potash. The salt of cobalt however appears to differ from the ammoniacal carbonate of cobalt described by M. Favre.—*Comptes Rendus*, June 16, 1851.

* In order to avoid the formation of the new salts described by M. Fremy at page 165.

On the Preservation of Alimentary Vegetable Substances. *By* M. Masson.

This process consists, first, in drying the matters at a moderate temperature in a stove for such time as is sufficient to expel the superabundant water which is not indispensable to the constitution of the vegetables, and then pressing them strongly in a hydraulic press.

The substances are first carefully picked, and the harder portions separated, as in the ordinary culinary method. They are next placed upon sieves of basket-work, or pieces of linen or canvas nailed upon a frame, and exposed to the action of hot air in a stove heated to about 118° F. for the most aqueous vegetables. A current of the heated air passes continually through the apparatus during the operation.

Some experiments were made by the Commission of the Academy to test the process.

920 kilogrms. of broccoli were picked, and yielded 725 kilogrms. of green matter for drying. After exposure in the drying apparatus for twenty-four hours to a temperature varying from 104° to 118° F., they were reduced to 69 kilogrms. of dry matter, having thus lost 656 kilogrms. of water, or 87 per cent. of their original weight. The other experiment was made with spinach. 820 kilogrms. of raw spinach were picked, and thus reduced to 639 kilogrms. of matter for drying. These in twenty-four hours were reduced to 71 kilogrms. of dry matter, having thus lost 89 per cent. of their weight. Pressure in the hydraulic press subsequently reduced the volume, bringing the density to 550 or 600 kilogrms. for the cubic metre.

The vegetables subjected to this process present a satisfactory odour and appearance, retain their flexibility and natural colour; and the form is so well kept in some, that they have the aspect of recently-gathered vegetables. When subsequently immersed in hot water, they absorb the principal part of the water lost during the desiccation. The following table exhibits the results thus obtained:—

Vegetable used.	Weight before immersion.	Temperature of the water.	Duration of the immersion.	Weight after immersion.	Proportion of weights before and after immersion.
Common cabbage..	280 grms.	122° F.	33^{m}	1·480	5·30
Brussels sprouts ..	139	122	38	0·630	4·53
Celery	130	122	41	0·510	3·93
Spinach.....	87	113	30	0·475	5·47

This mode of preservation of vegetables evidently offers peculiar advantages in its application to the use of the army and navy.—*Comptes Rendus*, May 19, 1851.

Occurrence of Mercury in Corsica.

An abundant deposit of pure cinnabar, which furnished 80 per cent. of mercury on analysis, has been discovered in the above island.—*Journ. de Pharm.*, March 1851.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On some Salts of Mesaconic Acid. *By* M. Pebal.

The acid employed in these experiments was prepared according to the method recently described by Prof. Gottlieb (p. 233), and purified by frequent recrystallization from hot solutions, which, owing to its sparing solubility in cold water, is connected with scarcely any loss. By a not too rapid distillation of 2 lbs. of citric acid, and, after separating the itaconic acid by crystallization, treating the citraconic acid obtained with dilute nitric acid, on an average $1\frac{1}{2}$ oz. of pure mesaconic acid was obtained. To be certain of its purity, it was submitted to analysis, when it furnished—

Carbon	45·80	45·96	10 =	60	46·15
Hydrogen	..	4·66	6	6	4·62
Oxygen	..	49·38	8	64	49·23

Experiments on the solubility of mesaconic acid gave the following results:—

100 parts of water at 64° F. dissolve....	2·7	parts	mesaconic acid.
100 parts of water at 212° F. dissolve ..	117·9	...	...
100 parts of alcohol of 0·833 at 63° F...	30·6	...	...
100 parts of alcohol of 0·833, boiling ..	95·7	...	...

When a hot saturated solution of mesaconic acid is let cool slowly (which is best done in a large water-bath), the mesaconic acid separates in very slender silky needles. When, on the other hand, a spirituous solution is boiled and evaporated to dryness on the water-bath, brownish laminæ are obtained, the colour probably arising from slight decomposition. The above numbers therefore can only be regarded as approximatively correct. I never observed this turning brown with aqueous solutions of pure mesaconic acid.

As well known, mesaconic acid fuses at 406° F., and then immediately sublimes. The sublimed acid furnished—

Carbon	45·41	10 =	60	46·15
Hydrogen	4·65	6	6	4·62
Oxygen	49·94	8	64	49·23

The difference in the amount of carbon is probably owing to the presence of small quantities of products of the decomposition of the acid, which was also indicated by the brown residue left in the

beaker from which the acid had been sublimed. Now since anhydrous mesaconic acid, $C^{10}H^4O^6$, would require 53·57 C and 3·57 H, it is evident from this experiment that mesaconic acid cannot be deprived of its hydrate water by a high temperature.

Neutral Mesaconate of Baryta, $2BaO, C^{10}H^4O^6 + 8Aq$, is obtained by saturating a boiling solution of mesaconic acid with carbonate of baryta. When the acid is not very pure, the solution acquires a yellow colour, which it communicates to the crystals, and is only very imperfectly removed by recrystallization; boiling with animal charcoal takes it entirely away. When the concentrated solution is left to spontaneous evaporation, beautiful transparent crystals, some lines in size and with a vitreous lustre, are formed; they are pretty readily soluble in water, and the solution is neutral to test-paper. They belong to the monoklinometric system. At 212° they part with the greater portion of their water of crystallization, becoming opake; but it is difficult to remove the whole of it at 212°. Dried at 266°, the salt furnished on analysis:—

Carbon	22·29	..	10 =	64	22·64
Hydrogen	1·70	..	4	4	1·51
Oxygen	18·01	..	6	48	18·11
Baryta	58·00	57·35	2	153	57·74

The air-dried salt furnished 21·07, 21·33, 21·17 = 8 equivs. water of crystallization; theory requires 21·36.

Acid Mesaconate of Baryta, $2(BaO, HO, C^{10}H^4O^6) + 3Aq$.—It is exceedingly difficult to obtain this salt in a state of purity, which is partly owing to the sparing solubility of the acid in cold water, and partly to the loose state of the combination.

When a solution of mesaconic acid is divided into two portions, the one saturated with carbonate of baryta and then united with the other, there is obtained, after decolorization with charcoal and suitable concentration, either verrucous crusts of crystals or six-sided prisms, with a lustre of mother-of-pearl, according to circumstances which I could not discover. I once found with the above crystals prisms, which, from their decided similarity to those of the neutral mesaconate of baryta which were formed in a mixture of mesaconate of baryta and mesaconate of potash, I did not hesitate to believe consisted of the neutral salt.

As it was proved by many experiments that the crystals of the acid salt tenaciously retained free acid, which could not even be entirely removed by recrystallization, I treated the pulverized crystals in one case with boiling, in another with cold alcohol. The salt treated in the first manner and dried contained 48·76, the other 46·4 per cent. of baryta, an amount which comes near to that of the neutral salt. The combination is therefore so feeble, that even alcohol at the common temperature removes a great portion of the acid.

Although I spared no pains to obtain the salt in a pure state, I have succeeded but very imperfectly, and merely enumerate a few of the results which come nearest to the probable composition of an acid baryta salt of mesaconic acid, by no means concealing the

fact that I obtained in the analysis of similar crystals, results which entirely differed. The air-dried salt furnished—

Carbon	28·67	28·53	..	20	=120	28·43
Hydrogen	3·31	3·36	..	13	13	3·08
Oxygen	32·19	31·28	..	17	136	32·22
Baryta.....	35·83	36·83	36·86	2	153	36·27

The salt dried at 284° lost 6·24–6·57 per cent. water of crystallization; the formula requires 6·4.

Neutral Mesaconate of Silver, $2AgO, C^{10} H^4 O^6$.—When a cold solution of mesaconic acid, carefully neutralized with ammonia or a dilute solution of neutral mesaconate of baryta, is mixed with nitrate of silver, a caseous precipitate resembling chloride of silver falls, soon acquires a granular consistence, and is obtained pure by washing with cold water and pressure between bibulous paper. It consists of microscopic crystals, is sparingly soluble in water, more readily soluble in the mother-liquor, and acquires, on treatment with hot water, especially with the action of light, a reddish colour. Heated somewhat quickly, the salt is violently decomposed, the silver being left in bulky vermiform masses. Dried *in vacuo*, the salt furnished—

Carbon.....	17·33	17·28	10 =	60	17·43
Hydrogen.....	1·43	1·18	4	4	1·16
Oxygen.....	18·44	..	8	64	18·59
Silver	62·80	..	2	216·3	62·82

The air-dried salt does not decrease in weight at 212°; its formula is therefore $2AgO, C^{10} H^4 O^6$.

On evaporating the liquid from the above precipitate, some very minute, shining, slightly-blackened crystals separated, which contained no baryta. Their weight was not decreased at 212°, and they left on calcination 61·95 per cent. of silver; they are therefore undoubtedly identical with the above silver salt.

On mixing an aqueous solution of mesaconate of soda with nitrate of silver, a precipitate falls which does not differ from the one above described; but upon the addition of alcohol to the liquid filtered from it, a very bulky transparent precipitate was formed, which did not become granular even after long standing, and when separated from the mother-liquor, shrunk to an amorphous mass. Washed with alcohol, pressed between blotting-paper and dried over sulphuric acid, it left on calcination 60·23 per cent. of silver. There can scarcely be a doubt that this salt is represented by the formula $2AgO, C^{10} H^4 O^6 + 2Aq$.

Acid Meconate of Silver, $AgO, HO, C^{10} H^4 O^6$, was prepared by dissolving the neutral silver salt in a boiling solution of mesaconic acid. An excess of the latter should be avoided, as otherwise it adheres to the acicular crystals of the acid salt, which separate as the solution cools. The salt is pretty soluble in hot water, is not coloured by exposure to the light, and when heated exhibits a similar behaviour to the neutral silver salt. Dried at 212°, it furnished—

Carbon	25·03	10 =	60·00	25·30
Hydrogen	2·24	5	5·00	2·11
Oxygen	27·14	8	64·00	26·98
Silver	45·59	1	108·15	45·61

Neutral Mesaconate of Lead, $2PbO, C^{10}H^4O^6+3Aq$, is obtained in a pure state by precipitating a solution of mesaconic acid, neutralized by ammonia, with acetate of lead, and also by precipitating neutral mesaconate of baryta with nitrate of lead, carefully washing the precipitate, and pressure between blotting-paper. The precipitate from solutions at the ordinary temperature is white, crystalline, very sparingly soluble in water and in the solution of neutral mesaconate of baryta, but readily soluble in a solution of nitrate of lead, on which account it is advisable in the preparation to pour the solution of the latter salt into the solution of the mesaconate of baryta, and not *vice versâ*, and to avoid an excess of the first salt. If this is present, no further precipitate is produced upon the addition of mesaconate of baryta, unless it be added in very considerable quantity.

But if, on the other hand, the liquids are mixed at a temperature near the boiling-point, the lead salt forms a resinous tenacious mass, which adheres to the sides of the vessel, and on cooling becomes solid and brittle. When once it has become solid, the salt does not reacquire its tenacious consistence on being heated with water.

When the liquid filtered from the precipitate is further evaporated, or, in the case of the tenacious precipitate, the hot liquid set aside to cool, neutral mesaconate of lead crystallizes out in short needles.

When the salt is heated, it puffs up strongly, and burns like tinder, leaving a residue of oxide and metallic lead. 100 parts of the salt, dried at 266°, furnished—

Carbon	17·44	..	..	10 =	60·00	17·89
Hydrogen	1·28	..	..	4	4·00	1·19
Oxygen	19·51	..	..	8	64·00	19·08
Lead	61·77	61·56	61·91	2	207·48	61·84

The following determinations of the amount of water of crystallization were made with salts which had served in part for the above analyses; they were all prepared with cold, or nearly cold solutions of mesaconate of baryta and nitrate of lead:—

$2PbO, C^{10}H^4O^6$..							335·48 = 92·55
3Aq.....	7·36	7·25	7·33	7·43	7·86	7·84	27·00 7·45

The tenacious salt and the precipitate from mesaconate of ammonia by acetate of lead furnished the following numbers:—

$2PbO, C^{10}H^4O^6$	..	..	335·48 =	94·91
2Aq	5·63	6·12	18·00	5·09

leading to the formula $2PbO, C^{10}H^4O^6+2Aq$.

Acid Mesaconate of Lead, $PbO, HO, C^{10}H^4O^6$.—The neutral lead salt is mixed in a dish with water, heated to boiling, and mesaconic

acid added until the greater portion of the salt is dissolved. From the filtered solution the acid salt crystallizes on cooling in small colourless needles, which are separated from the mother-liquor, treated with cold alcohol to remove any adherent mesaconic acid, and pressed between blotting-paper. When heated, mesaconic acid first sublimes, and then it behaves like the neutral lead salt. The air-dried salt did not decrease in weight up to 212°, and furnished—

Carbon	25·87	10 =	60·00	25·78
Hydrogen	..	5	5·00	2·15
Oxygen	..	8	64·00	27·50
Lead	44·68	1	103·74	44·68

Acid Mesaconate of Ammonia.—When a solution of mesaconic acid neutralized with ammonia is boiled, ammonia continues to escape for some time, and there then separates from the concentrated solution, crystalline agglomerations of the acid mesaconate of ammonia, which are readily soluble in water. The air-dried salt lost no water at 212°, when it furnished 40·66 C and 6·10 H; theory requires 40·81 and 6·12.

Mesaconate of Potash, prepared by saturating the acid with carbonate of potash, is very readily soluble in water, much less so in alcohol, and separates from a very concentrated aqueous solution, after long standing, in slender silky needles.

Mesaconate of Soda, prepared in the same manner, is very soluble in water, and crystallizes in very short four-sided prisms with truncated ends.

An experiment to prepare a salt from neutral mesaconate of baryta and sulphate of potash, in which 1 equiv. baryta was replaced by potash, did not succeed.

Mesaconate of the Oxide of Æthyle.—Mesaconic acid was distilled in a retort with twice the amount of an æther-mixture of sulphuric acid and alcohol of 0·833—required according to theory for the production of mesaconic æther, until the residue became black. The distillate contained sulphuric æther and some mesaconic æther. As but a small portion of the mesaconic acid had combined with æther, more alcohol was added to the residue in the retort, the mixture distilled, and this operation repeated until so little mesaconic æther resulted that it appeared useless to continue the process. After removing the sulphuric æther by heating in the water-bath and purifying the residue by distillation with water, the acid mesaconic æther was gently heated with carbonate of soda, washed with water, and dried by means of chloride of calcium. It furnished on analysis, in which a current of oxygen was employed,—

Carbon	57·85	18 =	108	58·06
Hydrogen.....	7·52	14	14	7·53
Oxygen.....	34·63	8	64	34·41

Mesaconic æther is a very mobile colourless liquid, of an agreeable fruity odour and a bitter taste; its specific gravity was found to be 1·043 at 68°; it distils unaltered; its boiling-point is constant at 428° with a barometric pressure of 730 millims. It is sparingly

soluble in cold, somewhat more easily in hot water, from which it separates on cooling, rendering it turbid; it mixes in every proportion with alcohol and æther, and does not redden blue litmus-paper. Mesaconic æther is not altered by gaseous ammonia.

As citraconanile is produced by heating mesaconate of aniline, the æther was boiled with barytic water, in order to be certain that no similar transformation of the acid had resulted in the formation of the æther.

I obtained, after complete decomposition and removal of the excess of baryta by a current of carbonic acid and warming, a salt of baryta, which possessed all the properties of the mesaconate. The acid separated from it by sulphuric acid behaved exactly like mesaconic acid. When hydrochloric acid gas is passed into an alcoholic solution of mesaconic acid, the neutral æther is likewise formed. A portion of the mesaconic acid employed always remained uncombined; but it was not possible to prepare the acid compound of mesaconic acid with oxide of æthyle.

According to the above, in the neutral salts of mesaconic acid, 1 equiv. water in the compound $C^5 H^3 O^4$ is replaced by bases, which hydrate water cannot be removed by heat, the hydrous acid subliming. Although it was impossible to prepare a double salt or an acid æther of this acid, I consider the proved existence of an acid silver and lead salt of the form MO, HO, $C^{10} H^4 O^6$, as sufficient reason for regarding mesaconic acid as bibasic, the theoretical composition of which would be expressed by 2HO, $C^{10} H^4 O^6$. It consequently appears to be isomeric with citraconic acid, from which it is derived, but differs essentially from it both in its hydrated state and in its salts.

Mesaconic acid is sparingly soluble in water at the ordinary temperature, on which account the salts crystallized from water readily have free acid adhering to them, which however, except in the case of the acid baryta salt, can easily be removed by treatment with cold alcohol. All the salts are soluble in water, most readily those of the alkalies; the neutral salts of silver and lead are sparingly soluble; their solubility increases with the temperature. The tendency to form neutral salts appears in mesaconic acid to be predominant; no basic salts were observed. The acid salts, on being heated, first part with free acid until with the increase of the temperature they carbonize, except in the case of the silver salts; and the separated carbon, especially in the baryta salts, is very difficult to burn. All the salts, except one of the silver salts, are obtained either as crystalline precipitates or in crystals.—Liebig's *Annalen*, May 1851.

On some Conjugate Compounds of Cobalt. *By* Dr. A. Genth.

The author has prepared a series of compounds of the sesquioxide of cobalt, $Co^2 O^3$, which resemble the series of platinum bases discovered by Gros, Reiset and Magnus.

When the protochloride or the protosulphate of cobalt is mixed with a large quantity of chloride of ammonium, then supersaturated

with ammonia, the mixture exposed to the air for four or five weeks until the free ammonia has escaped, hydrochloric acid then added until it has an acid reaction, and the mixture boiled, a heavy carmine-coloured powder falls. The mother-liquor contains a second orange-coloured salt. In this operation a conjugate compound, $Co^2 O^3, 3NH^4$, has formed, which behaves like a metal.

The Carmine-coloured Salt, $Co^2 O^3, 3NH^4 Cl$, is the chlorine compound of this cobalt base. It is sparingly soluble in cold, more readily soluble in boiling water. If this has been previously mixed with an acid, the solution is decomposed by ebullition or long standing. This decomposition does not occur with an addition of hydrochloric or acetic acid, and the salt may therefore be readily crystallized.

Concentrated sulphuric acid decomposes it on the application of heat, and dissolves the ammonio-sulphate of the protoxide of cobalt; concentrated hydrochloric acid decomposes it slowly on ebullition; it dissolves in hot concentrated nitric acid; hydrochloric acid precipitates it unaltered from the solution.

The compound crystallizes in forms belonging to the regular system. The crystals are small, of a peach-blossom to black colour; by transmitted light, carmine-red. They furnished on analysis—

Chlorine	42·49	3 =	1329·9	43·72
Ammonium	23·23	3	675·0	22·19
Sesquioxide of cobalt	33·50	1	1037·2	34·09

Ammonio-cobaltic Oxide.—The preceding chlorine compound, when treated with oxide of silver, parts with its chlorine. A substance dissolves in the liquid, to which it imparts a purple colour and a strong alkaline reaction; it is soon decomposed into ammonia and hydrated oxide of cobalt.

Carbonate of the Ammonio-cobaltic Oxide is formed in the treatment of the chloride with carbonate of silver. The solution of this compound is soon decomposed; it has a strong alkaline reaction, and dries under the exsiccator to a gummy mass. An acid carbonate appears also to exist.

Sulphate of the Ammonio-cobaltic Oxide is obtained by decomposing the chloride with sulphate of silver. The nitrate separates in crystals belonging to the klinorhombic system, and are of a purple or cherry-red colour. The chromate is crystalline, and of a dark orange colour; the molybdate forms a peach-blossom-coloured precipitate.

The chlorine compound enters into combination with the perchloride of mercury, and the double salt crystallizes in pale rose-coloured rhombic prisms, which easily separate into their components. Perchloride of tin produces in the acidified solution of the chloride a pale peach-blossom-coloured precipitate, consisting of silky needles. By recrystallization it is obtained in minute rhombic prisms.

A double salt with the bichloride of platinum, $Co^2 O^3, 3NH^4 Cl + 2PtCl^2$, is precipitated from solutions of the chloride upon the

addition of bichloride of platinum; it is sparingly soluble in cold, more readily in hot water. The salt crystallizes from the solution like the tin salt. It furnished on analysis—

Ammonium	8·58	..	3 =	675·0
Chlorine	40·91	..	7	3103·1
Platinum	33·39	..	2	2464·0
Sesquioxide of cobalt	13·70	15·07	1	1037·2

In the analysis of the chlorine compound, the author observed in the tube used for burning the salt with soda-lime, that some small lavender-coloured octahedra had formed. He thinks that they correspond to the crystalline protoxide of nickel described by him in 1846.

The Orange-coloured Salt is obtained in rhombic or klinorhombic crystals. It is very sparingly soluble in hydrochloric acid, which precipitates it from its solution in water. It was not easily altered by dilute hydrochloric acid, ammonia and boiling. With bichloride of platinum it furnishes a yellow double salt, which crystallizes in silky needles. The phosphate crystallizes in golden needles of great lustre; the chromate resembles croconate of potash. The author has not yet analysed any of these yellow salts. They are decomposed on ebullition with caustic potash, ammonia being eliminated, and the hydrate of the protoxide of cobalt precipitated.—Keller and Tiedemann's *Nordamer. Monatsbericht*, ii. p. 8.

ANALYTICAL CHEMISTRY.

√ *New Test for the Nitrites and Nitrates. By* G. C. Schæffer.

Chemistry has hitherto furnished no distinctive test for the nitrites when present in small quantities. From the supposed unfrequent occurrence of these salts, the want of such a test has never been felt.

For several years I have been engaged in a research which has led me to believe that the nitrites are of far more frequent occurrence than is commonly supposed, and that they have been mistaken for nitrates, as the usual process, with pure sulphuric acid and protosulphate of iron, will give the same reaction with both classes of salts. In order to settle the question, it was necessary to find a distinctive test, which should avoid all risk of confusion. I first tried acetic acid, which, as is well known, does not act upon the nitrates, while it decomposes nitrites. By substituting this acid for the sulphuric in the usual process, I succeeded perfectly. The test seemed even more delicate than that for the nitrates, and was more elegant in its operation.

Still the following difficulties were to be encountered. The slightest quantity of peroxide in the sulphate gave a colour with acetic acid, and injured the delicacy of the test. Moreover, the nitrites are generally either destroyed or converted into nitrates with

such readiness that it would be almost impossible to concentrate their solutions.

At last I was led to the following process, which leaves nothing to be desired. To the solution supposed to contain a nitrite, add one or two drops of solution of yellow prussiate of potash; there should not be enough to give a perceptible tinge to the liquid. A few drops of acetic acid are then to be added, and immediately, or in a few minutes, according to the quantity of nitrite present, the liquid assumes a rich yellow tint.

As the reagents used give nearly the same colour, spontaneously after some time, even in pure water, it is better, when testing for minute quantities, to use two similar vessels, one containing pure water and the other the liquid under examination, to both of which the reagents are to be added in precisely equal quantities. The vessels should be equally exposed to the light, with a sheet of white paper behind them.

With these precautions, I have found this test astonishingly delicate, in fact ranking with those for iron, iodine, &c. Using fused nitre, I have detected the presence of 1 pt. in 617,000 pts. of water, a by-stander, wholly ignorant of the nature of the operation, pronouncing as to the colour. Yet this salt contained about one-half its weight of undecomposed nitrate.

It should be remarked, that the presence of a large quantity of nitre has no influence upon this test, as with pure water it gives no colour. The same reaction answers also for the hyponitrates.

The next step is to convert this test into one for the nitrates. The decomposition of the nitrates of lead and mercury by boiling with excess of their respective metals has long been known. The reaction of metals with the alkaline nitrates does not seem to have been studied. I find that nitrate of ammonia is readily decomposed in presence of metallic lead; and what seems surprising, nitrate of potash is also decomposed, though not so readily.

To test for the nitrates, we have only to agitate the slightly-warmed liquid for a few minutes with shavings of lead, and proceed as before. By a longer digestion, more of the salt would be converted into nitrite, and the colour would be stronger. In estimating the delicacy of this process, I had used pure rain-water, but before completing the experiments I was obliged to be absent for several days; on my return, I soon found that the water from the same cistern contained so much of nitrates and nitrites, that it could no longer be used. From the readiness with which the decomposition was effected, I presume that nitrate of ammonia was present. The interval had been marked by the occurrence of frequent and severe thunder showers.

By using distilled water, I have been able to detect the presence of 1 part of nitre in about 60,000 of water, digesting with lead for only a short time. Mercury containing a minute quantity of lead seems to answer better than lead for a time in the above process, but after long use it loses its effect. It will not answer to add to it

any perceptible quantity of lead, as the liquid then becomes muddy on agitation.

Oxalic, tartaric and dilute hydrochloric acids may be substituted for the acetic, except when they produce precipitates, which would destroy the clearness of the liquid.

The yellow colour produced in this test is the result of a complex decomposition. Everitt's yellow salt and red prussiate seem to be formed, and in some cases also very minute quantities of Playfair's nitroprusside.—*Proceedings of the American Association, Newhaven*, 1851, p. 403.

On the Tests for Nitrates, and a new one for Nitrites.

By David S. Price, Ph.D., F.C.S.

My attention having been directed to the detection of nitric acid in cases where, if it existed at all, its quantity could be but small, I deemed it necessary, as a preliminary step, to ascertain the merits of some of the tests usually adopted for that purpose. The experiments were confined chiefly to two reactions, generally considered the most susceptible for nitrates; the one where the indication of the presence of nitric acid is the production of a dark violet or brown colour, caused by adding a solution of protosulphate of iron and concentrated sulphuric acid to a solution of a nitrate; the other, where it is the destructive action of nitric acid on indigo, the solution of the nitrate being made slightly acid with sulphuric acid, and then a solution of sulphate of indigo added. Before however detailing the results I have arrived at with respect to these tests, I shall proceed to describe a new one that has suggested itself for nitrites, but which admits, under certain circumstances, of application also for the detection of nitrates. Thinking that the addition of dilute hydrochloric acid to a solution of a nitrate in presence of iodide of potassium and starch-paste might cause the chlorine thus liberated to act in the nascent state on the iodide, and so produce the well-known blue colour, I tried the experiment, and found it to answer apparently most successfully. I was however surprised to find that of several nitrates employed, that of potash was the only one with which the experiment succeeded; furthermore, that hydrochloric acid was not at all a necessary condition for the production of the blue colour, oxalic, dilute sulphuric, and even diluted nitric acids effecting the same, whilst the same diluted acids produced no change in a simple mixture of iodide of potassium and starch-paste. It was therefore evident that the action was not dependent on chlorine, but on some substance to be found in nitrate of potash, and which will be demonstrated by the following experiments.

On distilling a few grains of nitre dissolved in 5 oz. of water with a small quantity of concentrated sulphuric acid, a distillate was obtained of slightly acid reaction, which when neutralized with carbonate of potash and concentrated, and then added to a mixture of iodide of potassium, starch-paste and dilute hydrochloric acid, was

found to produce a much deeper blue colour than did a concentrated solution of the original nitrate. This led me to try the effect of the nitrites on the same test-mixture, and which I found to possess the property of liberating iodine under the circumstances described in a most remarkable degree, and which must be attributed to the reduction of hydriodic acid by nitrous acid. On subjecting the nitrate of potash employed for the foregoing experiments to recrystallization, the crystals then obtained were found to have entirely lost the property they originally possessed, whilst the mother-liquor retained it in a high degree, clearly showing that the peculiar action of the nitrate of potash was to be attributed to the presence of a small quantity of nitrite. It has been shown that a very distinct indication of nitrous acid was obtained in the distillate from ordinary nitre and sulphuric acid; in order to see if such would be the case with small quantities of pure nitre when treated with pure sulphuric acid, I repeated the experiment, employing 2 grs. of the pure salt, 6 oz. of water and $\frac{1}{2}$ an oz. of concentrated sulphuric acid, when, after treating the distillate in the manner before described, abundant proof was afforded of the presence of nitrous acid. In all cases therefore where distillation is necessary in searching for nitrates, this test may be indirectly applied for them. Those substances which interfere with the formation of iodide of starch under ordinary circumstances prevent its production also by the present test. The method of employing the test is the following:—A few drops of a dilute aqueous solution of iodide of potassium (free from iodate) are mixed with a little starch-paste, and then dilute hydrochloric acid of specific gravity 1006 added. The liquid suspected to contain a nitrite, if alkaline, must be slightly acidified with hydrochloric acid, and then added to the test-mixture, when, if much nitrite be present, a dark blue colour will be instantly produced; and if very small traces only, then the liquid first assumes a pale fawn colour, which gradually changes to that of violet, plum, and ultimately dark blue. The extraordinary delicacy of the test will be seen from the following experiments. When water containing only the $\frac{1}{1,000,000}$th part of nitrous acid (as nitrite of soda, NaO, NO^3) is added to the test-mixture, a violet colour is almost instantly produced; with the $\frac{1}{1,500,000}$th part, the colour makes its appearance in a few seconds; with the $\frac{1}{2,000,000}$th part, after the lapse of two or three minutes; with the $\frac{1}{4,000,000}$th part, a change may be observed in twelve minutes; and with the $\frac{1}{5,000,000}$th part, a violet tint is produced in about fifteen minutes. In all these cases, the liquid rapidly assumes a dark blue colour. By performing the experiments in a porcelain basin, the faintest indication of colour may be observed. In searching for minute traces in a very large bulk of liquid, it is advisable to add more iodide of potassium than where the volume of the liquid is small. Since performing these experiments, I find that Schönbein* has noticed the action of nitrites on iodide of potassium.

With respect to the tests for nitrates specified at the commence-

* J. Pr. Chem. xlv. p. 227.

ment of the paper, De Richemont* has found that by the employment of the first one he was able to detect the $\frac{1}{24,000}$th part of nitric acid in a solution. The one by means of indigo has had narrower limits assigned to it; Liebig†, who suggested it, states that the $\frac{1}{200}$th part of nitric acid may be recognised by it, and the $\frac{1}{500}$th part when a little chloride of sodium is added. I shall endeavour to show, that in both cases the action is in all probability due to nitrous acid contained either originally in the substance as nitrite or produced by the action of sulphuric acid upon the nitrate; at any rate, that nitric acid in the cold has no apparent action upon either of them. And first, as regards the test with sulphate of protoxide of iron. If sulphuric acid be added to a solution of nitrate of potash free from all nitrite, and briskly agitated with it, so as to prevent the mixture from becoming heated, and then a solution of sulphate of protoxide of iron added, no change whatever in the colour of the liquid will ensue, even when allowed to stand for some time, which could not be the case did the action of the test depend on nitric acid. If to the same mixture one drop of a dilute solution of nitrite of potash be added, a brownish colour will be immediately produced, showing the instantaneous effect of nitrous acid upon the test. If, instead of keeping the mixture of nitrate of potash and sulphuric acid cold, we gently warm it, and then add a solution of protosulphate of iron and a few drops more of concentrated sulphuric acid, a dark violet colour will immediately appear, accompanied by an energetic disengagement of gas; the colour in this case soon disappears, owing to the heat evolved, but can readily be reinstated by a fresh addition of the protosulphate of iron. Or again, if we first add a solution of protosulphate of iron to the solution of the nitrate, and then pour in the concentrated sulphuric acid in such a manner that it forms a layer at the bottom of the vessel, we shall find that a violet colour will be produced at the contact-surface of the two liquids; the heat in this, as in the former case, being sufficient to cause the formation of nitrous acid. In searching therefore for small quantities of nitrates, it is advisable to add, as recommended by De Richemont, a large bulk of concentrated sulphuric acid. With respect to the delicacy of this test for nitrites, I have found that a liquid containing the $\frac{1}{5000}$th part of nitrous acid (in the form of a soda salt) becomes immediately coloured green upon the addition of a small quantity of sulphuric acid and sulphate of iron; that perceptible shades of green are produced when a liquid contains the $\frac{1}{500,000}$th, and a faint colorization with the $\frac{1}{1,000,000}$th part. In like manner to the preceding test, I have found that a solution of pure nitrate of potash, which has been treated in the cold with concentrated sulphuric acid or decomposed with tartaric acid, has no action whatever upon a solution of sulphate of indigo, but that the presence of the smallest quantity of nitrous acid is sufficient to destroy the same. By applying heat to the mixture of sulphuric acid and solution of nitre to which a few drops of indigo-solution have been added,

* Graham's Chemistry, p. 297. † Gmelin's Handbuch der Chemie, i. p. 813.

the colour of the latter will be found rapidly to vanish, and the test then becomes an exceedingly delicate one for nitrates, and in the absence of chlorates and organic matter may be most advantageously employed for them. I have examined the delicacy of the test for nitrites, and have found that the one, two and three millionth part of nitrous acid in a solution may be detected by means of it.

By all the foregoing tests it will be found that the sulphuric acid of commerce, as well as most kinds of carbonate of potash, contain a trace of nitrous acid. In conclusion, I may state that I have applied the nitrites to the detection of the iodides, the results of which experiments will be found in the accompanying communication.—*Quart. Journ. of Chem. Soc.*, vol. iv. p. 151.

On a new Test for Iodides. *By* David S. Price, Ph.D., F.C.S.

Having in the preceding paper pointed out the principle on which the detection of nitrites by means of iodide of potassium and hydrochloric acid depends, I shall proceed briefly to describe the application of nitrites for the detection of iodides, and at the same time give one or two instances of the practical application of the test in cases where the quantity of iodine is exceedingly small.

The method of employing the test is the following. The liquid suspected to contain an iodide is mixed with starch-paste and acidified with hydrochloric acid; a solution of nitrite of potash is then added, when, if much iodine be present, a dark blue colour will be instantly produced; if a very small quantity only, as for instance the two or three millionth part, then a few seconds elapse before the blue colour makes its appearance. In this manner I have detected the $\frac{1}{5,000,000}$th part of iodine dissolved in water as iodide of potassium. It will be seen that the test admits of a degree of delicacy not attainable by any of the other methods for detecting iodides, as well as being at the same time free from the disadvantages to which they are more or less subject; as, for instance, in the employment of chlorine, which, unless added very carefully to a liquid containing a trace of an iodide only, is almost sure to afford a negative result, from the chlorine combining with the iodine, and so preventing its acting on the starch. The same error may also arise by the use of nitric acid should the suspected liquid contain a large amount of chlorides.

I will now detail the two cases in which I have applied this test, in the one for the purpose of detecting iodine in cod-liver oil, the object being to see how small a quantity of the oil would suffice; in the other for the purpose of detecting iodine in marine vegetation. One ounce of ordinary brown cod-liver oil was saponified by a concentrated solution of caustic potash, and then carbonized in an iron spoon over an open fire; the residue was removed into a covered porcelain crucible, and strongly heated, so as effectually to destroy all organic matter, and when cold was digested with a small quantity of water, and thrown upon a filter; the filtrate, being acidified with hydrochloric acid, was then mixed with starch-paste, and tested

with nitrite of potash, which almost immediately produced a pale plum colour.

Sea-water contains so small an amount of iodine, that it is exceedingly difficult to detect even a trace of it in the mother-liquor from several pounds of water. Minute as this quantity must be, it is nevertheless collected and assimilated by many marine plants, and the following experiment enables us to demonstrate its presence in their juices. If we take a thin transverse sectional slice of the stem of the *Fucus laminaria digitata*, moisten it with a little starch-paste and dilute hydrochloric acid, and examine it by the aid of the microscope, we shall, upon adding a drop of a solution of nitrite of potash to the same, be able most distinctly to observe the formation of iodide of starch. The presence of an iodide may be shown in a still more marked manner, by suspending the stem of the same plant in a dry atmosphere, when the surface, after the lapse of some hours or days, will become covered with numerous transparent crystals, which on examination will be found to consist principally of chlorides, but at the same time to contain so much of an iodine compound as to impart an intense blue colour to the test-mixture.

Many marine plants, when placed in a fresh state in contact with the test-mixture, impart an orange colour to it, owing to the liberation of bromine.—*Quart. Journ. of Chem. Soc.*, iv. p. 155.

PROCEEDINGS OF SOCIETIES.

Royal Institution.

June 6, 1851. (The Duke of Northumberland, President, in the Chair.) The following paper was read :—

"Suggestions for the Dynamics of Chemistry derived from the Theory of Ætherification." By Professor Alexander Williamson, University College, London.

The human mind is only capable of understanding complicated phænomena when prepared by the study of simpler ones; and one of the most remarkable illustrations of this necessary order is afforded by the preparation of dynamical laws by the consideration of statical facts. In statics we consider phænomena in a state of rest, while in dynamics we study their change; and this distinction has been concisely stated by saying that the transition from the statical to the dynamical point of view consists in superadding the consideration of *time* to that of space.

To represent the unknown cause of any change in phænomena, the word FORCE has been formed, and is generally retained until the law of that change has been discovered; so that the dynamics of a subject may be said to constitute the explanation of the phænomena belonging to it.

It unfortunately often occurs that names are mistaken for explanations, and people deceive themselves with the belief, that, for in-

stance, in attributing chemical decompositions to affinity, attraction, contact-force, catalysis, &c., they explain them.

But owing to the necessary dependence of investigations on our mental operations, there is always a deficiency of facts corresponding to the imperfection of theory; that is, we only seek and see those facts which are more or less connected with our theoretical notions, and in most cases shut our eyes to such cases as appear contrary to them. This is peculiarly the case with chemical theory and chemical facts at the present day; for our atomic theory represents only certain simple and definite proportions of combination, and our researches have been fruitful in the investigation of such cases alone, the number of compounds of which we know nothing, being infinite, compared to those definite ones which we have studied.

In fact, it is certain that if we could sufficiently disengage our minds from preconceived notions on the subject, we should view those substances, which by more or less troublesome processes we separate out from the bodies presented to us by nature, rather as exceptional and artificial products than as the most normal and natural.

The lecturer submitted, that the definite compounds hitherto exclusively acknowledged and studied by chemists are in truth only exceptionally simple cases of combination, and that the consideration of chemists is only limited to them, because the atomic theory is as yet purely statical. The atomic theory has hitherto been tacitly connected with an unsafe and unjustifiable hypothesis, namely, that the atoms are in a state of rest; the dynamics of chemistry will commence by the rejection of this supposition, and will study the degree and kind of motion which atoms possess, and reduce to this one fact the various phænomena of change, which are now attributed to occult forces. But although it will probably be generally used in connexion with the atomic theory, the fact of motion is independent of any particular theory; and however the properties of matter may be conceived, it will remain true, that a change of place among the representatives or possessors of these properties is constantly going on, which produces the phænomena of chemical combination.

Chemical science has proved the indestructibility of matter, but it has yet to prove the indestructibility of motion or momentum by showing its transfer and dispersion among atoms.

There are many *primâ facie* evidences that *time* is necessary for chemical action; but this fact, although it has been noticed, has not as yet entered into the explanation of phænomena.

The one instance in which a certain regular motion of the constituents of a mixture was first proved, is the process of ætherification, of which the anomalous character has long since attracted the attention and study of many of the most eminent chemists, and has given rise to various theories, which respectively represented part of the phænomena.

The lecturer referred to the importance of having a correct stand-

ard of comparison for the various chemical groups or molecules, and briefly alluded to the evidence afforded by the formation of the intermediate æthers, that alcohol and various bodies allied to it have of late years been incorrectly represented comparatively to metallic oxides and æthers, and that the weight of alcohol which is truly equivalent to æther or water is not 46 but 23.

Having proved by a direct experiment that the formation of æther from alcohol is effected by substituting æthyle ($C^2 H^5$) for one-sixth of the hydrogen of that body, the process of ætherification by sulphuric acid was explained by a diagram, on which half the hydrogen in sulphuric acid was shown to change places with its analogue æthyle in alcohol; and that the peculiarity of the process, *i. e.* its continuity, is owing to this change of place between hydrogen and æthyle first taking place in one direction and then in the opposite; that is, that sulphuric acid becomes sulphovinic acid by taking up æthyle instead of an atom of hydrogen, and that it is then reconverted into sulphuric acid by resuming hydrogen instead of this æthyle, the first change forming water, the second æther.

By using successively two different alcohols, it was shown that the two steps of this decomposition can be separated and their reality proved. The process of ætherification is thus effected by a succession of double decompositions, each of which, considered individually, is perfectly conformable to the law of definite proportions; but the alternation and continuous succession, so clearly proved in them, is a fact unexplained by that law. A complete analogy between this process and the more familiar cases of chemical action is therefore only to be established by finding in these latter a similar atomic motion.

A little reflection is sufficient to show that such a motion actually exists. The fact of diffusion is in reality nothing but a change of place between atoms, effected by the mere action of the particles on one another; and there are many mechanical evidences of the communication of momentum from masses to atoms, and inversely.

It seems perhaps difficult to reconcile the apparent rest of the constituents of a mass with the existence of a continuous atomic motion; but there are many cases in which a rapid and continuous motion produces to our senses the appearance of a phænomenon at rest; thus the rapid revolution of a white sphere produces the appearance of a circle at rest when seen in front, and that of an ellipse when viewed obliquely.

There are, of course, many points of view from which the motion of atoms may be considered; but it is inasmuch as it produces or facilitates decomposition that the chemist has to regard it. We have in ætherification an evidence of the tendency of atoms of analogous nature to change places continuously; and it is natural to suppose that the facility of this interchange must be greater in proportion to the analogy between the molecules, and greatest between like molecules. The lecturer expressed a confident hope that he would soon be able to give a direct experimental evidence of this conclu-

sion, and proceeded to show how the admission of it explains, without the supposition of occult forces, the occurrence of double decompositions and the action of masses.

The exchange of analogous particles actually constitutes double decomposition; and its occurrence in alternately-opposite directions causes the two substances used to alternate with the two other compounds formed by the exchange of their bases; so that in such a mixture four substances are constantly to be found, the quantity of each substance corresponding to the average number of atoms which, in each moment of time, are in that state of combination.

Now it is clear, that if an equal number of atoms of a hydrogen salt and of an iron salt, reacting on one another, form a certain amount of the products of their double decomposition, a greater number of those products will be formed by doubling the quantity of the hydrogen salt; for the facility of interchange of iron with hydrogen remaining the same, the atoms of the iron salt will then come more frequently in contact with those of the hydrogen compound. Thus, on mixing a solution of sesquichloride of iron with sulphocyanide of hydrogen, a deep red colour gave evidence of the interchange of iron and hydrogen, forming sulphocyanide of iron and hydrochloric acid; but this exchange was not an operation effected once for all on the decomposing substances just coming in contact, but is constantly going on in the mixture; and the quantity of the products of this interchange remains constant, because a similar double decomposition, equal in absolute number of atoms per unit of time, is constantly going on between these products, reproducing the original compounds. In evidence of this, the counterpart of the decomposition of sesquichloride of iron by hydrosulphocyanic acid was shown in the expulsion of this last acid by hydrochloric, proved by the gradual diminution of the red colour on adding hydrochloric acid.

It is well known that caustic soda expels ammonia from its salts. But ammonia also expels soda; for it was shown that a mixture of ammonia and hydrochlorate of soda dissolves less chloride of silver than the same quantity of ammonia alone; and consequently that a saturated solution of chloride of silver in aqueous ammonia is precipitated by dissolving chloride of sodium in it. The same occurs with the ammonio-sulphate of copper.

In conclusion, the lecturer referred to the question of the relative velocity of transfer of analogous atoms in opposite directions, which necessarily determines the proportion of the elements of two salts, contained in the form of their products of double decomposition, on these salts being mixed. On the mixture of equivalent proportions of a couple of salts in aqueous solution, a certain amount of decomposition ensues, forming two other salts, and the chemical force may be considered proportional to the quantity of one couple compared to that of the other. Now as the proportion is only kept up by the number of exchanges in the one direction being *absolutely* the same in each moment of time as those in the opposite direction, it is clear that the relative velocity of interchange must be greatest be-

tween the elements of that couple of which the quantity is least; and chemical force must be inversely proportional to the velocity of these interchanges.

British Association for the Advancement of Science.—Meeting held at Ipswich, July 2nd, 1851.

On Agricultural Chemistry, especially in relation to the Mineral Theory of Baron Liebig. *By* J. B. Lawes *of Rothamsted and* Dr. J. H. Gilbert*.

Mr. Pusey had, in a recent article in the Journal of the Royal Agricultural Society on the Progress of Agriculture during the last eight years, quoted the experiments of Mr. Lawes and Dr. Gilbert as being conclusive against the "mineral theory" of Baron Liebig, which asserts that the crops upon the farm rise and fall according to the supply within the soil of the mineral constituents indicated by an analysis of the ashes of the plant. To these observations by Mr. Pusey, Baron Liebig has replied at some length in the new edition of his 'Letters on Chemistry' just published; and, in doing so, has asserted that the experiments alluded to are without value, and that the statements of the authors could only be made in ignorance of the rationale of agricultural practices on the large scale. The question at issue was an important one, for Baron Liebig, in the new edition of his 'Letters on Chemistry,' says of the agriculturists of England, that "sooner or later they must see that in this so-called 'mineral theory,' in its development and ultimate perfection, lies the whole future of agriculture."

The authors have therefore given in the present paper an outline of their investigations in agricultural chemistry, comprising an extensive series of experiments in the field, on the growth of the principal crops entering into a rotation, as well as upon the chemistry of the feeding of animals, and that of the functional actions of plants generally, in relation to the soil and atmosphere; in connexion with all of which branches much laboratory labour has constantly been in progress since the commencement of the experiments themselves in 1843. The results selected by Mr. Lawes and Dr. Gilbert in justification and illustration of their views, were those of the field experiments on wheat, grown *continuously* on a previously-exhausted soil for the last eight years, and in each season by means of many chemical manures, by the side always of one or more plots unmanured, and one manured continuously by farm-yard manure.

Some of the results thus obtained were illustrated by a diagram, from which it appeared that *mineral manures* had scarcely increased the produce at all when used alone, whilst the effects of ammoniacal salts were very marked, even when repeated year after year upon the same space of ground from which the entire crop, corn and straw, had been removed. Indeed in this way a produce had been obtained, even in the sixth and seventh successive years of the ex-

periment, exceeding by nearly two-thirds that from the unmanured plot. It was thus shown that the *mineral* constituents of the soil continued to be in excess *relatively* to the nitrogen available for them from natural sources. The history of several plots was then traced down to the last harvest (1850); and it was argued that the statements assailed by Liebig, namely that *ammonia* was specially adopted as a manure for wheat, was fully borne out when speaking of agriculture as generally practised in Great Britain; in other words, that in *practice* it was the defect of *nitrogen* rather than of the *mineral* constituents which fixed the limit to our produce of corn.

The authors next called attention to the fact of the exhalation of nitrogen by growing plants, as proved by the experiments of De Saussure, Daubeny and Draper; and they referred to some experiments of their own, with the view of showing the probability that there is more of the nitrogen derived from manure given off during the growth of the cereal grains, than by leguminous and other crops; and hence might be explained the great demand for nitrogenous manures observed in the growth of grain. The authors suggested that here was an important field of study, and that we have in the facts alluded to much that should lead us to suppose that the success of a rotation of crops depended upon the degree in which the restoration of the balance of the *organic* constituents of the crops was attained by its means, rather than on that of their *mineral* constituents, according to the theory of Liebig; whilst the means adopted to secure the former were always attended with a sufficient supply of the latter.

Again, Professor Liebig has quoted the processes of fallowing and liming, as being in their known results inconsistent with the views of Mr. Lawes and Dr. Gilbert; but these gentlemen considered that the experiments of Mulder, and of Mr. Way on the properties of soils, justified them in supposing that the processes of fallowing and liming owed their efficacy more to the accumulation of *nitrogen in the soil* from natural sources than to that of available mineral constituents. The latter did however undoubtedly thus accumulate by these processes; and this fact should give us more confidence in views, which, on independent evidence, supposed that they were not so easily liable to be found in defect in relation to other necessary supplies.

It was next shown, by reference to what happens in actual practice, as generally followed in Great Britain, where corn and meat constitute almost the exclusive exports of the farm, that the mineral constituents of the crops taken collectively, that is as shown by the analysis of their ashes, could not be considered as exhausted. Of these however phosphoric acid was lost to the farm in much larger proportion than the alkalies; whilst the latter would generally, by the combined agencies of disintegration of the native soil and import in cattle-food, be liable to a diminution in but a very insignificant degree, if not in some cases to accumulation. Practical agriculture had indeed decided that phosphoric acid must be returned to the land from sources external to the farm itself, viz. by bones,

guano, or other means; but, on the other hand, artificial alkaline manures had generally been found to fail in effect.

Indeed, taking into careful consideration the tendency of all experience in practical agriculture, as well as the collective results of a most laborious experimental investigation of the subject, both in the field and in the laboratory, it was the authors' deliberate opinion, that the analysis of the crop is no *direct* guide whatever as to the nature of the manure required to be provided, in the ordinary course of agriculture, from sources *extraneous to the home manures of the farm*, that is to say by artificial manures.

Reviewing then the actual facts of practical agriculture, the authors could not agree with Baron Liebig when he asserted that our grand object should be to attain an artificial mixture to *substitute* for farm-yard manure, which he admitted to be the universal food of plants. The very practice of agriculture itself, as followed in this country, necessitated the production of farm-yard manure, and all our calculations should be made on the supposition of its use. That it was not a *substitute*, but an *adjunct*, that was the great desideratum; and this would never be attained by theoretical considerations, in which no distinction was made between those constituents which are only taken from the field to be returned to it in due course by the home-manures of the farm, and those which are actually sent off the farm. This distinction was however seldom, if ever, made by chemists unconnected with practical agriculture; and to this cause may in great part be attributed the reiterated recommendations to imitate in artificial manures the composition of the ashes of the plants to be grown.

In conclusion, then, if the mineral theory of Professor Liebig simply implied that the growing plant must have within its reach a sufficiency of the constituents of which it is to be built up, the authors fully and entirely assented to so evident a truism; but if, on the other hand, he would have it understood, that in the ordinary course of agriculture in Great Britain it is in relation to the mineral constituents collectively as found in their ashes that the soil would be exhausted, they did not hesitate to say that they were in ignorance of a single fact to favour such a view. On the contrary, they believed that *nitrogen* is the constituent most exhausted *relatively* to other constituents; that of the *minerals*, *phosphoric acid* is exhausted more than the alkalies; and further, that the apparent demand for an artificial supply of manurial substances for the production of crops in *agricultural quantity, itself an artificial process*, is frequently greater than can be accounted for by the mere idea of supplying the actual *constituents* of the crop. If, then, we would attain by the aid of science a rational system of agriculture, the actual facts of the art itself, together with a study of the functional actions of plants and animals, must receive a due share of our attention. In fact, chemistry *alone* will do nothing for practical agriculture *.

* For the above abstract we are indebted to Dr. Gilbert. We defer our notices of the other communications brought before the Chemical Section to our next Number.—Ed.

THE CHEMICAL GAZETTE.

No. CCXII.—August 15, 1851.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On Uroxanic Acid, a Product of Decomposition of Uric Acid. *By* G. STÆDELER.

THE decomposition of some nitrogenous acids from the animal secretions (hippuric acid and the acids of the bile) into non-nitrogenous acids and nitrogenous compounds closely related to urea having proved successful, it was not improbable that uric acid, by suitable treatment, would likewise experience a similar decomposition. I have therefore submitted the behaviour of this acid towards potash and hydrochloric acid to closer examination; and although my expectation, that, like hippuric acid, it would assimilate 2 atoms of water for each equivalent of nitrogen, and so split up into urea and a bibasic non-nitrogenous acid $=2HO+C^6H^2O^8$, therefore closely related to mesoxalic acid, has not been realized, I have nevertheless observed another simple decomposition of it, which appears to me not less interesting.

Uric acid is scarcely acted upon by concentrated hydrochloric acid. After long-continued boiling, chloride of ammonium can, it is true, be detected in the liquid; but the amount is so inconsiderable, that it must appear doubtful whether it has been produced by the decomposition of the uric acid or by the absorption of ammonia from the atmosphere.

Uric acid is likewise but slowly acted upon by caustic potash. On heating a solution of it in an excess of tolerably concentrated potash for some days nearly to boiling, and replacing from time to time the water evaporated, a slight decomposition was evident from the constant disengagement of a minute quantity of ammonia; but even after eight days the solution contained so large an amount of uric acid, that I lost all hope of being able to attain complete decomposition in this way; I therefore placed the solution aside. By the absorption of carbonic acid, biurate of potash soon separated in the form of a white powder, and after about four weeks, some shining tabular crystals, which continually increased, were formed, whilst the urate redissolved. From 8 to 10 grammes of uric acid had been used for this experiment, and yet it took more than half a year before the precipitate had entirely disappeared and the crystals had formed in sufficient quantity to allow of their examination.

These crystals are the potash salt of a new acid, which, for reasons which I shall subsequently mention, I shall call *uroxanic acid.*

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The mother-liquor contains, besides some uroxanate of potash the potash salt of another nitrogenous acid, sparingly soluble in water, which separated upon the addition of sulphuric acid as a white crystalline powder, and dissolved like uric acid, with evolution of gas, in nitric acid; but it differed from it both by its solubility in ammonia, and from the solution in nitric acid not giving the characteristic red colour on evaporation, nor on moistening the residue with carbonate of ammonia. From the smallness of the quantity and its exceedingly great decomposability, it was impossible to submit it to more accurate examination. Besides these sparingly-soluble acids, the presence of oxalic, formic, lantanuric acids and urea were detected in the mother-liquor.

Uroxanic Acid is obtained by decomposing the potash salt with dilute muriatic or sulphuric acid. When a warm moderately-dilute solution of uroxanate of potash is employed, the acid sometimes separates in very beautiful, colourless, transparent tetrahedra, which however can only be distinguished with the aid of the microscope. By decomposing a concentrated or cold solution of the salt, it is usually obtained in short, imperfect, concentrically-grouped prisms.

It dissolves sparingly in cold water, plentifully on ebullition, but with decomposition and disengagement of carbonic acid. It is wholly insoluble in alcohol. When the acid which has been dried *in vacuo* is heated somewhat above 212° in a glass tube, there is a slight deposition of water, and carbonic acid is disengaged. When heated more strongly, it melts to a brown liquid, disengages ammonia, then furnishes an oily distillate, which solidifies on cooling, and apparently cyanide of ammonium, and finally leaves a small carbonaceous residue. Strong nitric acid has no action upon the acid in the cold; on the application of heat, it dissolves slowly without any evolution of gas; and on cooling, comparatively large, well-formed crystals separate, which appear to be a product of oxidation of the acid. On evaporating the solution to dryness, a white residue is obtained, which is not coloured by carbonate of ammonia. Dried *in vacuo*, it furnished—

Carbon	26·89	10 =	750	26·91
Hydrogen	4·17	9	112·5	4·04
Nitrogen	..	3	525	18·83
Oxygen	..	14	1400	50·22

From the analysis of the potash salt, it will be seen that it contains 3 equivs. nitrogen and 2 atoms of basic water, so that its composition is expressed by the formula $2HO + C^{10} H^7 N^3 O^{12}$. Consequently uroxanic acid is formed from uric acid by the assimilation of 8 atoms of water and the loss of 1 atom of ammonia—

$$\underbrace{2HO + C^{10} H^2 N^4 O^4}_{\text{Uric acid.}} + 8HO = \underbrace{2HO + C^{10} H^7 N^3 O^{12}}_{\text{Uroxanic acid.}} + NH^3;$$

and it might be viewed as a combination of the amide of formic acid with oxamic acid $= 2HO, C^2 O^3 C^2 O^2 NH^2 + C^2 HO^2, NH^2$, which would readily explain the occurrence of formic and oxalic acids in

the mother-liquor of the potash salt. With 6 atoms of water, uroxanic acid would be exactly resolved into 4 atoms of oxalic acid, 1 atom of formic acid and 3 atoms of ammonia.

It differs from alloxanic acid by containing the elements of 1 atom more formiate of ammonia—

$$2HO + C^8 H^2 N^2 O^8 + NH^4 O, C^2 HO^3 = 2HO + C^{10} H^7 N^3 O^{12}.$$

On heating an aqueous solution of alloxanic acid, decomposition and evolution of carbonic acid occur; the same is observed on boiling a solution of uroxanic acid. The connexion existing between these two compounds, which is likewise apparent in the salts, has induced me to form the name of this acid after that of alloxanic acid.

Unfortunately, from want of material, it has been impossible to trace further the decomposition which a solution of uroxanic acid experiences on ebullition; but from the composition of a product of metamorphosis, which is formed on heating the dry acid to 266°, and which I shall describe under the name of *uroxile*, I conclude that it consists simply in the uroxanic acid parting with the elements of 2 atoms of carbonic acid, and so passing into a new acid, the composition of which would be expressed by the formula $2HO + C^8 H^7 N^3 O^8$.

As urea and lantanuric acid were found in the mother-ley of the uroxanate of potash, it is not improbable that the action of potash upon the uroxanate has partially resolved the uroxanic acid into formiate of ammonia and alloxanic acid, and that the latter has experienced the known metamorphosis into mesoxalic acid and urea, and into lantanuric and carbonic acids*,

$$\underset{\text{Alloxanic acid.}}{2HO + C^8 H^2 N^2 O^8} + 2HO = \underset{\text{Mesoxalic acid.}}{2HO + C^6 O^8} + \underset{\text{Urea.}}{C^2 H^4 N^2 O^2}.$$

$$\underset{\text{Alloxanic acid.}}{2HO + C^8 H^2 N^2 O^8} + HO = \underset{\text{Lantanuric acid.}}{HO, C^6 H^4 N^2 O^6} + 2CO^2.$$

The acid precipitated from the mother-liquor by sulphuric acid may possibly have been leucoturic acid; but Schlieper states of that acid, that it is decomposed by nitric acid; and it is therefore possible that it may have been a peculiar hitherto-unknown product of decomposition of uroxanic or of uric acid.

* According to Schlieper, alloxanic acid is resolved, on heating its aqueous solution, into leucoturic acid, diffluane, carbonic acid and water. He admits that the decomposition extends to 2 atoms of alloxanic acid, and advances the following equation to explain the formation of these bodies:—

$$2(2HO + C^8 H^2 N^2 O^8) = C^6 H^3 N^2 O^6 + C^6 H^4 N^2 O^5 + 4CO^2 + HO;$$

but since, in this decomposition, leucoturic acid and diffluane are never obtained in the stated proportion, but the former always constitutes by far the smallest portion of the product; since, moreover, the description of diffluane applies much better to a mixture of lantanuric acid and oxalate of ammonia than to a pure compound; and, lastly, the production of the oxalate of ammonia may be readily explained from the composition of leucoturic acid,—there can scarcely be a doubt that the formation of these two bodies takes place independently; and that, therefore, according to the above formulæ, the alloxanic acid is decomposed, on the one hand into lantanuric and carbonic acids, and on the other into leucoturic and oxalic acids.

Uroxanate of Potash.—Prepared as above described, it separates in oblique four-sided prisms with truncated edges, frequently half an inch in size. From the roughness of the lateral surfaces, an accurate measurement of the crystals was impossible; but according to an approximative determination the acute angles are 83°, and the obtuse 97°. It has a strong mother-of-pearl lustre, dissolves pretty readily in cold, and very abundantly in hot water, but not in alcohol. When the aqueous solution is mixed with alcohol, a white crystalline precipitate is instantly formed, which renders the solution pasty even when moderately concentrated. If it be then gently heated, the precipitate redissolves; and on cooling, the potash salt separates in delicate plates, which present exactly the form of the original salt under the microscope; no acid salt therefore appears to be produced in this manner. The aqueous solution of the uroxanate of potash has a neutral reaction, and is not decomposed by ebullition. When the salt is dried at 212°, it loses water and becomes milk-white; at a higher temperature, it melts, gives off carbonate of ammonia, which is deposited in crystals in the colder part of the tube, and finally leaves a residue coloured by carbon. The analysis of the salt, dried over chloride of calcium, led to the following results:—

Carbon	17·20	10 =	750	16·99
Hydrogen	3·88	13	162·5	3·68
Nitrogen	12·60	3	525	11·89
Oxygen	40·03	18	1800	40·76
Potash	26·29	2	1177·8	26·29

After two hours' drying at 212° it lost 13·98 per cent., and after three hours more it had lost altogether 14·79 per cent. The formula of the salt is therefore $2KO + C^{10} H^7 N^3 O^{12} + 6Aq$. 5 atoms of water of crystallization amount to 12·74, 6 atoms to 15·29 per cent. Consequently uroxanate of potash contains 6 atoms of water, of which it readily loses, like the alloxanate, 5 atoms at 212°, whilst the sixth atom is tenaciously retained.

Uroxanate of Ammonia.—Uroxanic acid dissolves readily in dilute ammonia; and on mixing the ammoniacal solution with alcohol until turbidness results, the compound soon falls in small, imperfect, oblique four-sided prisms.

Uroxanate of Baryta.—When the ammoniacal solution of the preceding salt is mixed with chloride of barium and a little alcohol, it immediately separates in thick flakes, which soon change into slender shining needles.

Uroxalate of Lime is obtained like the baryta salt, but a far larger amount of alcohol is required before the solution becomes turbid; it then separates gradually in minute, shining, oblique four-sided prisms, which after some time are converted into larger crystals, perfectly similar to the baryta salt.

Uroxanate of Lead separates in delicate satiny scales, when the solution of the potash salt is mixed with a solution of nitrate of lead, until the existence of an acid reaction. The salt, dried over sulphuric acid, lost, on being heated to 212°, 2·22 per cent. of water of crystallization. It furnished—

	Found.	Calculated.
Oxide of lead.....	52·05	52·12
Acid	47·95	47·88

Consequently the formula of the salt is $2PbO + C^{10} H^7 N^3 O^{12} + Aq$.

Uroxanate of Silver is formed by decomposing the potash salt with silver, and separates as a white flocculent precipitate, which soon collects into a heavy amorphous powder. It turns red in sunlight; and when heated with the liquid, immediately becomes brownish, and then as black as coal.

Uroxile.—On heating uroxalic acid to 212°, a constant decrease in weight is observed; and even with the employment of a small quantity and raising the temperature to 266°, a considerable time is requisite before the weight becomes constant. The dazzling white colour of the acid disappears, the bulk gradually increases, and there remains at last a somewhat yellowish, coherent, hygroscopic mass, which furnished on analysis—

Carbon	29·82	8 =	600	29·81
Hydrogen	4·46	7	87·5	4·35
Nitrogen.....	..	3	525	26·09
Oxygen	..	8	800	39·75

leading to the formula $C^8 H^7 N^3 O^8$. It differs from uramile by containing 2 atoms more water, and I have therefore selected for it for the present the name of uroxile. Whether at a higher temperature it passes into uramile, I have not been able to determine, my whole stock of uroxanic acid being exhausted.

On comparing the above formula with that of uroxanic acid, it will be seen that the latter has lost 2 atoms of water and 2 atoms of carbonic acid to form uroxile—

$$2HO + C^{10} H^7 N^3 O^{12} = C^8 H^7 N^3 O^8 + 2HO + 2CO^2;$$

and if we assume that the lost water was the basic water of the acid, it becomes highly probable that the decomposition of the uroxanic acid, on boiling its aqueous solution, consists, as previously stated, in its losing the two elements of carbonic acid, but none of the basic water.

It is moreover remarkable that uroxile has the same composition as the dialurate of ammonia; since however the latter is changed at 212° into a blood-red mass, whilst uroxile is only produced at a high temperature, no nearer connexion between the two compounds can exist.—Liebig's *Annalen*, June 1851.

On the Ammonio-chloride of Magnesium. *By* W. S. Clark.

Chloride of magnesium is of itself not volatile. Hitherto no combination of it with ammonia was known; such a one however exists, and it is volatile. It was obtained in examining the behaviour of ammoniacal gas towards chloride of magnesium at the fusing-point of silver. The chloride of magnesium was placed in a porcelain tray in a porcelain tube; excepting a trace of magnesia, it was wholly volatilized, and condensed in the colder portion of the tube into

a white loose powder, which proved to be a compound of chloride of magnesium and ammonia, with the formula $MgCl+2NH^3$, viz.

	Found.	Calculated.
Magnesium	15·85	14·7
Chlorine	45·34	43·5
Ammonia	38·81	41·7

The want of agreement between the found and the calculated results is owing to the compound undergoing spontaneous decomposition, so that it cannot be weighed without a loss of ammonia. It appears to sublime only in a current of dry ammoniacal gas. Chloride of potassium, treated in the same manner, furnishes no such compound*. —Liebig's *Annalen*, June 1851.

On the Changes undergone by Animal Tissues.

By Prof. Rud. Wagner.

On the 14th of April 1851, Prof. Wagner laid before the Academy of Sciences at Göttingen a series of experiments, which he made in a morphological and chemical point of view, upon the alterations undergone by animal tissues. The first experiment consisted of a repetition of that formerly instituted by John Hunter and Berthold upon the transplantation of the testicles of fowls, and was made in conjunction with Prof. Leuckart. The result obtained differs in many points from those of the earlier experimenters. In these experiments a number of young fowls were operated upon, the testicles removed by abdominal section and detachment with the finger, as is usually done with capons, and one or two of the recently-detached testicles immediately taken from one fowl, and placed in the abdomen of another. The recently-removed testicles of rabbits and frogs were also inserted into fowls. Wagner subsequently extended his experiments still further; the testicles of fowls were introduced into other fowls, pigeons, and those of pigeons into fowls, and so on. The animals were then killed at the end of some weeks or months, and examined. The testes were found enveloped in plastic exudation, which was sometimes of a membranous consistence, sometimes converted into cellular tissue, permeated by fat, and furnished with vessels. At some part or other of the wall of the abdomen, the liver or the intestines, there was membranous adhesion. The testes were more or less atrophied, diminished in size, drier, and exhibited internally gradual destruction and disappearance of the seminal cells, spermatozoa and the vesiculæ seminales; and the microscope showed that a copious formation of fat had taken place, partly originating within the decomposing cells, partly free between them.

In the birds' testicles which had been introduced, there were found under the microscope, in addition to free fat and cells con-

* Prof. Wöhler observes, that magnesium is evidently a volatile metal. When heated in the air, it burns with a white flame like zinc, with formation of white fumes of magnesia.

taining globules of fat, aggregated globules of fat without envelopes, large granule-cells (inflammation-globules), small acicular crystals of fat, lime-salts, a few plates of cholesterine, masses of hæmatine, black pigment, and transition formations of the two colouring matters. Another experiment, in which the testicles of some rabbits were introduced into the abdominal cavity of a young fowl, showed that in twenty-four days the testicles had become puckered by false membranes, one of which on the left was adherent to the intestine, the other on the right to the wall of the abdomen. They had diminished unequally, one being reduced to a third part of its size, the other to nearly half, and they felt hard; the vas deferens had become a solid cord. Each testicle represented a hollow sac with walls, like the cyst of an encysted tumour, in every case with a smooth coating like a serous membrane. The cavity contained a loose yellow honey- or wax-like mass, which under the microscope appeared to consist for the most part of fat with some remains of epithelium. In consequence of this experiment bearing upon the question of the conversion of proteine-matter into fat, the author made the following experiment. A number of fresh testicles of frogs, cleaned as much as possible, were examined as to the amount of fat they contained; at the same time, similarly-prepared frogs' testicles were introduced into fowls, and after some months and weeks were again removed, separated from the cellular and fatty exudation-capsule surrounding them, and the amount of fat they contained also determined. Moreover, fresh crystalline lenses were introduced into the abdominal cavities of fowls and pigeons, and these killed after from ten to fifteen days.

According to Uhrlaub's analyses, in Wöhler's laboratory, of the lenses which had remained in the abdomen, a very considerable amount of fat was present; also in the testicles of the frogs, which (in winter) contained about 3 per cent., this amount of fat was augmented to 5–15 per cent. (calculated for the fresh testicles).

In these experiments, the following facts were observed in regard to the crystalline lenses. As in the case of all the other bodies, an envelope of exudation was formed, which soon became metamorphosed into a membranous capsule of varying thickness. Absorption and diminution of the substance of the lens soon followed. The lens of an ox, which when fresh weighed 2·825 grms., was within forty-three days reduced in weight to 0·528 grm.; the lens of a sheep, which weighed 2·640 grms., was reduced in forty days to 0·136 grm. In the case of two lenses, which were placed at the same time in the abdomen, and were fixed to different spots, the loss in weight was frequently very different. The internal changes experienced by the substance of the lenses were also frequently very different in equal times. Some lenses, even in three weeks, were thoroughly converted even as far as the nucleus, which resists the metamorphosis for the longest period, into a honey-yellow, more or less hard, or even greasy mass, whilst others exhibited on the surface only a yellow layer from 1 to 2 millimetres in thickness; and others, again, appeared still semitransparent, opakish-yellow, like the lenses

of old persons, but were of a gelatinous consistency. Microscopic examination then showed that the almost folded capsule of the lens was completely unchanged and perfectly retained its character of a structureless glassy membrane, as when fresh. The fibres of the lens were more or less broken up, the fragments distinctly recognizable, coated with small granules; and between them, small crystals of fats (margarine, frequently in glands, as in the chalaza-membrane of the hen's egg), granule-cells with fine molecules, smaller cells with nuclei and fatty granules (probably altered cells of the liquor Morgagni), larger globules combined into grape-like masses (aggregations of fatty globules), and frequently also large drops of a yellow fluid fat. Dried lenses also gradually underwent a fatty metamorphosis, but much more slowly, beginning at the circumference. In 0·222 grm. of the substance of the lens, which formed the residue of 5·98 grms. of fresh lens which had been kept for six weeks in the abdomen of a fowl, Uhrlaub found on analysis 47·86 per cent. of a yellow fat, of an agreeable odour. But this was the largest quantity. In a number of analyses which the author made, partly alone and partly in conjunction with Dr. Schröder, the fat amounted to only 7, 10, 14–15 per cent. of the dry substance of the lens. The eye of a scarcely half-grown white rabbit, perfectly free from pigment, was removed from the recently-killed animal, and immediately placed in the abdominal cavity of a strong young fowl. It weighed 1·544 grm. In fifty-four days the fowl was killed. The eye was situated between masses of fat behind the abdominal walls, surrounded by a membranous capsule, from which prolongations passed, some to the intestine, some to the abdominal walls. It now weighed 0·542 grm., and appeared completely atrophied. The lens was diminished in size, and formed a yellow mass with fatty agglomerations, the nucleus very hard, the fibres of the lens still preserved, and the capsule of the lens not changed. The cornea was very thick and opake. The sclerotica, the choroid and the retina, formed together an almost inseparable layer, in which insular masses of granular, red, blackish-brown and black colouring matter existed. Carefully-cleaned portions of the intestines of frogs, which were filled with coagulated blood of pigeons and calves, were introduced in the same manner as the substances treated above. In forty days, the blackish-brown, much-dried mass of blood exhibited accumulations of granular, reddish, bright red and reddish-brown colouring matter, partly surrounded with membranes resembling cells, as we so frequently meet with in the tissues of the human body. Similar accumulations of black pigment-granules to those in the lungs, more rarely surrounded by cell-membranes, here and there with a crystalline aspect, also frequently occur; also numerous large and small drops of fat, sometimes with large drops of a brown fat; in fewer number, small crystals of fat, single or in little heaps. Plates of cholesterine were found in very large number.

Pieces of well-cleaned muscular substance, free from fat, from the thigh of the frog, after remaining three weeks in the abdomen of a pigeon, became perfectly unrecognizable, and formed yellow

rounded bodies, appearing almost like the testicles of frogs which had become atrophied in the same manner. The thick wax-yellow mass exhibited, under the microscope, between the primitive muscular bundles, which were still recognizable, and more or less preserved, and especially in the centre, deposits of finely-granular fat, and in part also most beautiful large yellow drops of oil. Muscular tissue appears to be very easily and quickly converted into fat, with which, as is well known, pathological experience is also in conformity.

Boiled white of hens' eggs was introduced in separate pieces, and also examined after the lapse of three weeks. The pieces were partly solid, rounded, partly tender, especially the yellowest, frequently much resembling the altered lenses, interwoven with numerous larger and smaller yellow drops of oil, and between these, aggregations of fatty globule- and granule-cells. This metamorphosis of the structureless coagulated albumen also appears to show that the fatty metamorphosis does not emanate from the cells of the tissue.

The author remarks, in conclusion, that the method selected by him is particularly adapted for experiments of this kind, as these operations are not very painful to birds, and succeed much more readily than in the mammalia. In the course of the memoir, he draws attention to the circumstance that the capsule of the lens has not yet been examined by chemists.—*Nachrichten der Gesellsch. der Wissensch. zu Göttingen*, May 1851.

✓ *On a new Alkaloid from Opium.* *By* F. Hinterberger.

The author purchased as narcotine a substance which contained very little of that principle, but consisted for the greater part of a new alkaloid, whose composition is represented by the formula $C^{66}H^{36}NO^{23}$. The author has named it *opianine*.—Liebig's *Annalen*, lxxvii. p. 207.

✓ *On the Products of the Dry Distillation of Wood.*
By Dr. C. Vœlckel.

The author has examined those products of the destructive distillation of wood which are lighter than water. The crude material was obtained from Kottmann's manufactory of pyroligneous acid in Solothurn.

This oil has a yellowish colour, which passes after some time into brown, and has a peculiar odour. In order to obtain it colourless, it was distilled first with water, when it always passed over yellowish. At the commencement of the operation, oil with only a little water distils over, then oil and water in equal proportions, and lastly water with very little oil, whilst the residue contains a tarry mass of very disagreeable odour. In the water separated from the oil, acetic acid, wood-spirit, mesite, and other bodies which occur in crude wood-spirit, were found.

The oil purified by distillation with water, as it was evidently a

mixture, was submitted to distillation, and the product collected in separate portions. The oil begins to boil at 158° F., but the thermometer rises very rapidly, so that up to 266° only about an ounce had distilled over from a pound of oil. This was kept separate. From 266° the thermometer rises more slowly; the oil which passed over up to 320° was collected apart, as also that from 320° to 401°, at which temperature the whole of the oil had distilled over. All three portions were of a yellowish colour; each portion was examined separately.

The first portion, the oil which boiled between 167° and 266°, could not be purified by treatment with an aqueous solution of caustic potash; on the other hand, when an equal volume of potash dissolved in absolute alcohol is mixed with the oil, it acquires a dark brown colour; and if, after long contact, the oil is distilled off with addition of water as soon as the greater portion of the alcohol has passed over, it is obtained colourless and of an agreeable ætherial odour. From the residual potash acids separate a small quantity of a brown tarry substance. On a second treatment of the oil with the alcoholic solution of potash, the liquid was coloured but slightly yellowish. The clear colourless oil was freed from alcohol, a trace of ammonia and of a volatile organic base, by washing first with water containing sulphuric acid, and then with pure water; it was dehydrated over chloride of calcium and distilled. The oil begins to pass over below 212°, but perfect ebullition does not occur before 221°, the thermometer constantly ascending; the oil which passed over up to 230° was collected separately, likewise that portion of the oil which distilled over between 230° and 248°, as also that between 248° and 266°. Each of these three portions of oil was submitted to fractionated distillation, but it was not possible to obtain an oil with a constant boiling-point. The author therefore has only made the following analyses in order to ascertain its composition; the oil analysed was certainly a mixture, which, as shown by the analyses, does not possess the composition of olefiant gas, but comes near to that represented by the formula $C^{24} H^{32} O^{3}$.

The oil has the following properties:—It is clear, colourless, very mobile, has an ætherial odour and a burning taste, and burns with a luminous somewhat smoky flame; its specific gravity is 0·841. It is only slightly soluble in water, but mixes in every proportion with alcohol and æther; it is entirely destroyed by concentrated sulphuric acid, and converted into a brown resin, with the simultaneous formation of a conjugate sulphuric acid, without any production of sulphurous acid, when the mixture of oil with sulphuric acid has been carefully made so as to avoid the generation of much heat. The oil is likewise violently acted upon by concentrated nitric acid, and converted, with evolution of red vapours, into a yellow resinous mass, which remains dissolved in the acid, and is separated by mixing with water. It furnished on analysis—

Carbon	78·18	77·99	24 =	1800	78·26
Hydrogen	8·95	8·88	32	200	8·69
Oxygen	12·87	13·13	3	300	13·05

The oil which distilled over between 230° and 248° agrees almost entirely in its properties with the preceding, except that the odour is somewhat different and the specific gravity a little higher, =0·846. It is likewise destroyed by concentrated sulphuric acid, but water separates along with the resin a very small quantity of oil, which can be distilled off. Towards strong nitric acid it behaves like the preceding. The analyses of this portion of the oil led to the composition $C^{30}H^{40}O^{3}$, as follows:—

Carbon	80·45	80·17	30 =	2250	80·36
Hydrogen	8·95	8·97	40	250	8·93
Oxygen	10·60	10·86	3	300	10·71

Carbon and hydrogen stand here, as in the preceding analysis, in the relation of 3 to 4. From a comparison of the formula $C^{30}H^{40}O^{3}$ with the formula $C^{24}H^{32}O^{3}$, it is evident that the oxygen decreases in the oil, passing over at an increased temperature, whilst the proportion of carbon remains the same. The oil distilled over between 248° and 266° agrees with the preceding except in the odour and specific gravity, which is 0·851. In this case also analysis shows a decrease of oxygen, whilst the relation of carbon to hydrogen remains the same; it furnished 82·25 C, 9·22 H, and 8·53 O.

Second Portion of Oil.—The oil which passed over between 266° and 320° amounted to a third of the entire quantity employed; it is somewhat yellowish, and was treated, like the preceding distillate, with an alcoholic solution of potash to remove the colouring constituent. The mixture acquires a dark brown colour; after some time the oil was distilled off, but as it was not perfectly colourless, it was again treated with the alcoholic solution of potash. From the residue in the retort, acids separate a tarry substance with a disagreeable smell, from which a small quantity of creosote was separated by distillation with water. The oil which distilled over with alcohol and water, after removal of the first and washing with water, had an alkaline reaction and a stupifying odour, which arose from the presence of a small quantity of a volatile alkaloid, and disappeared on being agitated with dilute sulphuric acid. After the oil had been freed from the sulphuric acid by washing with water, it was dehydrated over chloride of calcium, then distilled and collected in several portions. That which passed between 266° and 284° is clear, colourless, very mobile, has an ætherial odour resembling that of the preceding oil, and burns with a luminous smoky flame; its specific gravity is 0·853; it mixes in every proportion with alcohol and æther. It furnished on analysis 83·72 carbon, 9·37 hydrogen, 6·91 oxygen.

Nitric acid acts violently upon the oil, concentrated sulphuric acid much less so; from the brown-coloured mixture, water separates resin with a little oil.

The oil which distilled over between 284° and 302° agreed almost entirely with the preceding. Its specific gravity was somewhat higher, viz. 0·857; it furnished on analysis 84·21 C, 9·55 H, 6·24 O.

The portion of oil which passed over between 302° and 320° had

a specific gravity of 0·865. In other respects it did not differ from the preceding portion, and gave on analysis 84·97 C, 9·86 H, 5·35 O.

The analyses of the oils which passed over between 266° and 320° show, like the oils which distilled over between 221° and 266°, a constant relation of the carbon to the hydrogen of 3 : 4.

Strong nitric acid acts less violently on those oils which distil over between 284° and 320° than on those which are volatilized at a lower temperature. A large portion of the oil is destroyed, it is true; but a portion of it, although a small one, swims undecomposed upon the acid, and is only converted into resin after long action. Concentrated sulphuric acid acts in a similar manner. In this case likewise a portion of the oil floats upon the acid, coloured brown by the destruction of the remainder of the oil.

Third Portion.—That portion of the oil which passed over between 320° and 401°, amounting to somewhat more than a half of the whole, was submitted to the same process of purification as the second one. It was not possible to obtain it perfectly colourless and of a pure odour by the action of an alcoholic solution of potash, and subsequent distillation. The oil which passed over with the water, especially the latter portions, were always somewhat thick, yellowish, and accompanied with an odour which could no longer be removed by agitation with dilute sulphuric acid. On distilling the dehydrated oil, the first portions passed over colourless, but the last were always coloured, while at the same time there remained a small residue of a coloured resin. It was only possible to free it from this resinous substance by distilling it over some solid pieces of caustic potash, which became brown, while the oil passed over perfectly colourless and with a pure odour. The oil was now distilled alone, and the distillate collected in three portions as follows:—

I. Collected between 320° to 338°, spec. grav. 0·867
II. Collected between 347° to 374°, spec. grav. 0·871
III. Collected between 374° to 401°, spec. grav. 0·877

These three portions exhibit the greatest resemblance to each other; in their general properties they do not differ from those which distilled over at a lower temperature. They gave on analysis,—

	I.	II.	III.
Carbon	85·55	85·62	85·90
Hydrogen	9·70	9·70	9·73
Oxygen	4·75	4·69	4·37

In this case also the carbon stands to the hydrogen in the relation of 3 : 4.

The oils which passed over between 320° and 401° differ essentially in their behaviour towards concentrated nitric and sulphuric acids from those which distil over at a lower temperature. While the latter were violently acted upon even at the ordinary temperature, the action of the above acids upon the oils whose boiling-points are situated between 320° and 401° is considerably less at the ordi-

nary temperature. When concentrated nitric acid is mixed with one of these oils, the acid turns yellow, it is true; the greater portion however of the oil floats undecomposed upon the acid, and only after a long time does it begin to resinify; the decomposition is much assisted by heat. If this oil be agitated with strong sulphurous acid, a small portion is immediately dissolved by the acid; but the greater portion floats upon it, and disappears only after a long time.

Since on mixing oils with low boiling-points with concentrated sulphuric acid, only those containing oxygen are destroyed, the author adopted this treatment, adding the acid so that the mixture should not become heated. When an equal volume of sulphuric acid had been added, the mixture was frequently shaken, and after some time the oil drawn off, the brown thick acid again mixed with half its volume of sulphuric acid, and this operation repeated until the acid no longer acquired any colour. The oil, after being separated from the sulphuric acid, was washed with water, distilled with water and dehydrated. The clear, colourless, thin oil now exhibited an entirely different odour, resembling that of those oils which are formed in the distillation of resin, &c. The oil is insoluble in water, but readily soluble in alcohol and æther, and burns with a smoky flame. On distillation, it begins to pass over at 302°, and boils at 311°; the thermometer however constantly rises up to 400°, at which temperature the last portion of the oil passes over without residue. The distillate was collected in five portions, viz.

I. Between 302° and 320°, spec. grav. 0·864
II. Between 320° and 338°, spec. grav. 0·867
III. Between 338° and 356°, spec. grav. 0·871
IV. Between 356° and 374°, spec. grav. 0·877
V. Between 374° and 400°, spec. grav. 0·881

The five portions of oil furnished on analysis—

	I.	II.	III.	IV.	V.		
Carbon....	89·60	89·72	89·99	89·66	89·83	3=225	90·00
Hydrogen..	10·21	10·13	9·99	10·25	10·25	4 25	10·00

When the sulphuric acid is allowed to act long on these oils, and especially on the application of heat, conjugate acids are formed.

From the facts contained in this paper it results that the above oils are hydrocarbons with the relative proportion $C^3 H^4$, isomeric with mesitylene (œnole), and compounds of the same with oxygen.—Poggendorff's *Annalen*, lxxxii. p. 496.

On a new Compound of the Volatile Oil of Turpentine. By A. Sobrero.

The moist essential oil of turpentine rapidly absorbs oxygen under the influence of light. There is formed a crystalline compound, the composition of which is not susceptible of being expressed by any of the formulæ of the different hydrates of turpentine hitherto known. To obtain this substance, oxygen is passed into a receiver placed over water until four-fifths of the water are displaced, when the

essential oil of turpentine is introduced in sufficient quantity to form a layer of about half a centimetre in thickness. The whole is now exposed to the action of direct light, when very soon the inner surface of the receiver, which is not touched by the water, becomes coated with a crystalline substance in the form of minute prismatic needles, which gradually increase in size, and which in the course of some days are more than 1 centim. in length. At the same time the liquid is seen to ascend in the vessel, which would become filled if care had not been taken to arrange the apparatus so that the air might enter in proportion as the absorption took place. By arranging a series of vessels in this manner, a considerable quantity of this crystalline substance may be obtained.

To separate and purify this substance, the vessels are removed from the bath, and after the water and oil have been allowed to drain off, a little alcohol is poured in, which quickly dissolves the crystals. The united solutions furnish on evaporation the crystalline substance contaminated with oil of turpentine. It is purified by recrystallization from alcohol and from water.

This substance is inodorous; it is soluble in alcohol, æther and in water. From its boiling aqueous solution it separates in long prisms in stellate groups. When boiled with water slightly acidulated with sulphuric acid, it is decomposed into a volatile product, of an odour resembling that of the oil of turpentine and camphor. This character prevents its being confounded with the hydrate of turpentine of Wiggers, which under the same circumstances furnishes an oily volatile body, with the odour of hyacinth. It furnished—

Carbon.....	70·58	= 20
Hydrogen	10·58	18
Oxygen	18·84	4

Consequently its formula is $C^{20} H^{16} O^2 + 2HO$.—*Comptes Rendus*, July 21, 1851.

On Human Bile. *By* Dr. Enderlin.

The author has detected in the bile of a man who died of dropsy, cholalic acid and taurine. The presence of choloidic acid could not be proved with the same certainty. The blood contained urea, but none of the constituents of the bile could be detected in it.—Liebig's *Annalen*, lxxv. p. 162.

On the Presence of Arsenic and Antimony in Mineral Combustibles, in various Rocks, and in the Water of the Ocean. *By* A. Daubrée.

The occurrence of certain substances, even though in exceedingly small quantity, in rocks is interesting, not merely in a theoretical point of view of the distribution of the simple bodies of the crust of the earth, but on account of the part which they may act in their

relation to organized bodies. The occurrence of so active a poison as arsenic in various rocks appears to me deserving of notice.

In searching for fossils in the carboniferous limestone of Villé, Bas Rhin, in which hitherto none have been found, I observed a vast number of little crystalline granules, of a metallic-gray colour, which proved to be arsenical iron.

This distribution of arsenic in the carboniferous limestone induced me to look for the same substance in the seam of coal which is worked at a lower depth of 12 metres. The two principal varieties of this coal contain arsenic in the proportions of 0·169 and 0·415 grm. per kilogramme. Moreover this coal contains antimony and traces of copper.

This first result led me to seek for arsenic in other combustible minerals. The coal of Sarrebruck, the lignites of Bouxwiller and of Lobsann were found to contain an appreciable quantity of arsenic; the proportions contained in these three combustibles were found to be respectively 0·03, 0·037 and 2·09 grms. per kilogramme. This large amount of arsenic in the lignite of Lobsann accords with the circumstance, that the tertiary beds to which this lignite is subordinate likewise contain a deposit of iron ore, in which there is so much arsenic that it is not worth working.

A remarkably pure specimen of Newcastle coal furnished mere traces of arsenic and a determinable quantity of antimony. In fact, all the combustibles examined contained arsenic and antimony.

For examination, the minerals were treated with from 4 to 5 times their weight of nitric acid with 4 equivs. water, which was added gradually, and the whole kept in a state of ebullition. When the reaction was complete, the whole was evaporated to dryness, then digested with pure concentrated sulphuric acid, the liquid diluted with water was filtered, and then conveyed into a Marsh's apparatus. The arsenic was collected in the form of rings, stains, or condensed in a solution of nitrate of silver, according to the process of M. Lassaigne. All the reagents employed were ascertained to be perfectly free from arsenic.

Having found so large an amount of arsenic in these sedimentary strata, I was induced to seek for this substance in the two sources whence are derived the principal materials of the stratified rocks, viz. the eruptive rocks on the one hand, and the water of the ocean on the other. With 100 grms. of basalt from the Kaiserstuhl I found decided proofs of the presence of antimony in this rock; the kilogramme contains 0·01 of arsenic and 0·03 of antimony, or 30 grms. of arsenic and 90 grms. of antimony in a cubic metre.

It was probable that if the water of the ocean contained arsenic acid, this acid would become concentrated in the insoluble salts which are precipitated by evaporation. I therefore examined for arsenic the incrustations of the boilers of a steam-vessel trading between Havre and Malaga. I operated upon 1 kilogrm. of this crust, which was treated in a closed vessel with boiling concentrated sulphuric acid, in order to collect any arsenic which might be disengaged in the state of chloride. The excess of sulphuric acid was

partly neutralized with potash, which had previously been examined in Marsh's apparatus, in order to remove it by crystallization as sulphate of potash. With respect to the arsenic acid or the arseniate of potash which the liquid might contain, it ought, owing to its great solubility, to become concentrated in the mother-liquors. These were concentrated and introduced into Marsh's apparatus, when they furnished 9 milligrms. of arsenic, or nearly 0·000001 of the substance employed.

The results of these experiments show that arsenic is widely diffused in various rocks, where it is constantly accompanied by antimony. This distribution accounts for the presence of arsenic in the ferruginous deposits of numerous mineral springs, in which it was first detected by Prof. Walckner. The phosphorus which vegetables take up from the soil in order to convey it into the body of animals, is probably not contained in the rocks from whence it is originally derived in much greater quantity than arsenic, for it is only quite recently that the presence of phosphates has been ascertained in many rocks and minerals. If subsequent researches do not prove the presence of arsenic in vegetables, it must be admitted that the plant, while it assimilates the phosphorus, eliminates the arsenic, which is thus restricted to the inorganic kingdom by vital action.—*Comptes Rendus*, June 2, 1851.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Ipswich, July 2nd, 1851.

On the Growth of Plants in various Gases.

By Dr. J. H. Gladstone *and* Mr. G. Gladstone.

This paper was in continuation of the one read at the last Meeting of the Association, in which it had been shown that hydrogen gas was innocuous to plants. The same was now proved in respect to nitrogen, the contradictory results formerly arrived at having been explained.

It was also shown that pansies and grass plants, placed in atmospheres of pure oxygen, nitrous oxide or carbonic oxide, inverted over water, remained in a healthy condition for several weeks. Gaseous hydrocarbons also had no injurious effect, the experiments having been tried with bulbous-rooted plants. The general conclusion was, that, as far as plants are concerned, either of the great constituents of the atmosphere may prevail, to the exclusion of the other; or they may be replaced by other gases—hydrogen, nitrous oxide, carbonic oxide or carburetted hydrogen—without causing any immediate injury to the living organism. Plants, of course, cannot grow without a supply of carbon; yet the deprivation of their gaseous food appears, in very many instances, merely to cause

an indefinite suspension of their functions.—*Abstract communicated by the Authors.*

On Atomic Volume and Atomic Weight, with Considerations on the Probability that certain Bodies now considered as Elementary may be decomposed. *By* Prof. Dumas.

The author observed, that upon a comparison of the various substances reputed elementary, we are enabled to arrange them by certain resemblances into various well-marked groups; and those composing the same group are capable of substituting one another in compounds without altering the general character of the body. Such a group is the triad—chlorine, bromine, iodine. Now all the essential properties of bromine are intermediate between those of chlorine and iodine; and so is its atomic weight, the equivalent numbers of the three being 35, 80 and 125. Thus, could we by any means take half an atom of chlorine, and add it to half an atom of iodine, we might expect to produce bromine. Similar triads are found in sulphur, selenium and tellurium; lithium, sodium and potassium; and calcium, strontium and barium. M. Dumas, in illustration of his views, adverted to the analogous groups in organic chemistry, for instance the æthers; and drew attention to the fact of the several members of any one of these triads being generally found together.—*Literary Gazette*, August 9, 1851.

On the Chemical Nomenclature of Organic Compounds. *By* Dr. Daubeny.

The object of this paper was to point out certain inconsistencies and anomalies in the received method of classifying and naming organic compounds; and thus, if possible, to induce chemists to agree on a set of rules, by adhering to which the compositions and relations of a body might be inferred from the termination of the word designating it. The Professor first alluded to the nomenclature proposed by Gmelin, which imposed new names upon all known elements, and thus was at least as difficult as the acquisition of an entirely new language. Not conceiving that so intricate a system would ever come into vogue, he proceeded to point out the meaning belonging to the several terminations attached by eminent chemists to the names of bodies of their own discovery, as indicative of the class to which they belonged, and likewise their method of denoting the composition of a body by constructing for it a name made up of those expressive of its several ingredients. In order to introduce somewhat more of precision into this method of nomenclature, and also to render it in some instances more convenient and more applicable to daily use, the Professor submitted to the Section the following suggestions:—1. That the term *hydrocarbon*, when used to designate a class, should be confined to the compound radicals; the essential oils being regarded either in the light of hydrurets, from their containing an atom of hydrogen in a different state of combination from the rest, or of aldehydes, from their tendency to form acids by the addition of 2 atoms of oxygen. 2. That the term *æther*, as designating a class, should be restricted to the oxides of the re-

spective compound radicals; and that the "compound æthers" should be named on the same principle that salts are, by terms expressive of their respective acids and bases. 3. That the term *cetone* should be retained for bodies produced from acids by the abstraction of a single atom of carbonic acid; 4. and that of *glyceride* for fixed oils. 5. That the termination *yle* for compound radicals, and *ene* or *en* for carbohydrogens with equal atoms of the two elements, be retained. 6. That to the vegetable alkalies produced by natural processes the termination *ine* should be confined; and to those artificially produced by substitution of hydrocarbons for the hydrogen atoms of ammonia that of *amine*. 7. That the names proposed by Hofmann for the alkaloids of his own discovery should be abbreviated by introducing only the first syllable of the name expressive of each of the hydrocarbons present, by which expedient the length of the word so compounded need rarely exceed six syllables. 8. That the termination *amide* should be retained merely for bodies formed by the replacement of the hydrogen atoms *when they are not alkalian*; and that the terms *imide* and *nitrile* should be no longer employed. 9. That the termination *am*, occasionally used for ammonia compounds, be discarded. 10. That the termination *al* for aldehyde compounds should be henceforward employed with more precision. 11. That the termination *ethane* should be used for those æther compounds only into which an acid does not enter. 12. That the termination *an* should be employed in a more definite sense than heretofore. 13. That the terminations *one* and *ole* should be respectively confined, the former to bodies produced from acids by the abstraction of 1 atom of carbonic acid, and the second by that of 2 atoms; so that the latter term should not be adopted to indicate the essential oils. 14. That where a name expressive of the composition of a body cannot be constructed, one should be formed having reference to some obvious physical or chemical property, and of which the Greek or Latin root can be readily apprehended. Such barbarous and unmeaning terms therefore as mercaptan, kapnomor, pittacal, parabanic acid, &c., should be rejected from the vocabulary of science. 15. That bodies produced by natural processes should in general bear a name recalling the source from whence they are derived; 16, and lastly, That although bodies belonging to the same class or type should in general have the same termination, yet, that where a substance already familiar to us is shown to belong to a particular type, its designation ought not in that case to be altered, so as to bring it into harmony with the other bodies with which it may be thus associated.

The above suggestions are thrown out rather as embodying the views of the most eminent chemists, so far as these views can be inferred from their practice, than as expressive of any new methods or arrangements conceived by the author of the paper; and in the former light are submitted to the Chemical Section, with the hope that the whole subject may be taken into consideration by a committee selected from that body, to whose suggestions on such a subject men of science in general might be disposed to defer.—*Athenæum.*

PATENT.

Patent granted to Henry Grissell *and* Theophilus Redwood, *for Improvements in coating Metals with other Metals.*

For coating Iron with Zinc.—The patentees use a bath or vessel of suitable shape and size, in which the zinc is melted by the application of heat. On the surface of the melted metal is placed a thick stratum of chloride of zinc, made by dissolving zinc in muriatic acid, and applying heat until the whole of the water has been driven off, or a mixture of 8 parts of chloride of zinc and 10 parts of chloride of potassium, or a mixture of about equal parts of chloride of zinc and chloride of sodium, or a mixture of about equal parts of dry or anhydrous sulphate of zinc and chloride of sodium or chloride of potassium. When the zinc and the saline compound are in a state of fusion, the iron to be coated is put into the melted zinc through the fused salt, and is kept there for a short time. On taking it out, if the zinc has not adhered to all parts of it, some powdered salt ammoniac is to be sprinkled over it according to the usual method, and the immersion effected again.

For coating Zinc, Iron coated with Zinc, or other Metal, with a Metallic Alloy.—The alloy is melted in a bath or vessel by the application of heat. One of the alloys used consists of about 26 parts of tin, 10 parts of zinc and 5 parts of lead. A stratum of chloride of zinc mixed with about an equal weight of sal-ammoniac is kept in a state of fusion over the surface of the melted alloy, and more sal-ammoniac may be added from time to time if the salt becomes thick. Care must be taken not to apply more heat than is necessary to keep the alloy and the saline compound fluid. The metal to be coated is put through the saline compound into the alloy, but it should not be left there longer than is necessary for effecting the coating. The patentees also use the alloys commonly known as "fusible metal" in the same way as the preceding. The fusible metal preferred consists of bismuth, lead and tin, which may be mixed in the proportions of 8 parts of bismuth, 5 parts of lead and 3 parts of tin; but other proportions may be used provided the resulting alloy will melt at a temperature below 400° of Fahrenheit's scale.

For coating Iron or other Metal with Tin, or with Tin alloyed with Lead.—The tin, or alloy of tin and lead, is melted by the application of heat in a bath or vessel of suitable size and shape, which it is preferred should be made of iron; and a stratum of chloride of zinc, to which about an equal weight of sal-ammoniac has been added, is kept in a state of fusion over the surface of the melted metal. More sal-ammoniac may be added from time to time if the saline compound becomes thick. The iron or other metal to be coated is put into the melted metal through the salt which floats on its surface, and is kept there until the coating has been effected. It is found advantageous in conducting this process, and the same remark applies to the preceding processes, to pass the metal to be

coated several times into and out of the bath, so that the saline compound used may each time come into contact with the surface to be coated. It is also found advantageous, in the preceding processes, to put the metal to be coated into a boiling or hot solution of chloride of zinc, slightly acidulated with muriatic acid before putting it into the metallic bath.

For coating Iron or other Metal with Silver, or with an Alloy of Silver and Copper.—The surface of the iron or other metal to be coated is first amalgamated, which may be effected by any of the well-known processes for the purpose, but the following process is found to answer very well for amalgamating the surface of iron:—About 12 parts of mercury, 1 part of zinc, 2 parts of sulphate of iron, 2 parts of muriatic acid and 12 parts of water are mixed in a dish or pan to which heat is applied; and whilst the mixture is hot, say at a temperature of about 200°, the iron to be amalgamated is put into it, and the mercury spread or rubbed over the surface of the iron. The silver or alloy of silver and copper is melted in a crucible placed in a suitable furnace, and the amalgamated metal is put into it, and left there until the coating has been effected.

For coating Iron with Copper, with Brass, or with any Alloy of Copper, with Zinc, Tin or Lead.—The copper or alloy to be used for coating the iron is melted in a crucible placed in a suitable furnace, and a stratum of borosilicate of lead (made by fusing together about 24 parts of boracic acid, 112 parts of oxide of lead and 16 parts of silica) is kept in a state of fusion over the surface of the melted metal. The iron to be coated is put into the melted metal through the borosilicate of lead, and is left there for a short time, or until the coating has been effected.

Sometimes the iron is coated with zinc or with tin, or the surface amalgamated by the processes already described; and, when thus coated, introduced into the melted copper or alloy containing copper.

A coating of copper or of brass is also given to iron in the following way:—Chloride of copper is put into the bottom of a crucible or other suitable apparatus, and above it is placed the iron to be coated. The crucible is covered and put into a furnace, and kept at a red heat until the chloride of copper has volatilized, and the vapour coming in contact with the iron has left a coating of copper upon it. Instead of chloride of copper, metallic copper and sal-ammoniac or oxide of copper and sal-ammoniac may be used.

In order to convert the coating of copper thus produced into a coating of brass, some zinc is put into the bottom of a crucible, and over it some animal or other charcoal. The iron with its copper coating is then introduced, and the crucible filled up with the charcoal, and a cover closely luted on, with only a small aperture for the escape of gases. The crucible is now put into a fire, and heated to redness, so as to volatilize the zinc, the vapour of which coming in contact with the copper will combine with it to form brass.—Sealed Jan. 11, 1851.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

Observations on Lime, and on two new Combinations of this Base with the Sesquioxides of Iron and Chrome. *By* J. Pelouze.

The first indication of the existence of these new compounds was owing to accident. I was examining an earthy ore of iron containing a considerable amount of lime, and had made a solution of it in hydrochloric acid, and mixed it with caustic potash. I obtained a yellowish-white precipitate, which presented at first nothing particular, but which became perfectly white after some hours, and then by long exposure to the air passed into an ochreous red. This circumstance attracted my attention; and after several vain experiments to ascertain the cause of the phænomenon, I found at last that it was to be attributed to a combination of lime and peroxide of iron, the existence of which had hitherto remained unknown to chemists. I was able to reproduce this compound at will by precipitating directly with a solution of caustic potash certain atomic mixtures of a salt of lime and a salt of peroxide of iron.

When a quantity of perchloride of iron representing 1 equiv. of peroxide is dissolved in water, and mixed with 4 equivs. chloride of calcium, an excess of potash, poured into the mixture, produces a chamois-coloured precipitate, which becomes perfectly white in the course of a few hours, and retains this state permanently, provided it be protected from contact with the air. The precipitate formed by pouring a mixture of the salts of iron and lime into an excess of potash has the same colour, and also turns white after some time. This precipitate, washed with boiled water, only parts with potash to sugared water, and oxalate of ammonia merely produces a slight turbidity in the wash-waters; but if the precipitate, instead of being formed in the manner above described, is made in the presence of a larger proportion of the lime salt than 4 equivs. to 1 of the per-salt of iron, sugar-water removes a very considerable quantity of lime. This circumstance is explained from the composition of the new double oxide; it is formed of 1 equiv. peroxide of iron and 4 equivs. of lime.

The phænomenon of coloration, which the precipitate exhibits at the moment of its formation, is easily explained. A very small portion of the peroxide of iron is precipitated without uniting with the lime, whence the chamois colour, which completely disappears by

the subsequent and complete combination of the two bases. With respect to the red colour which the compound acquires by contact with the air, it is due to the action of the carbonic acid, which combines with the lime, and sets free the oxide of iron; and after sufficient exposure to the air, the whole of the lime occurs in the state of carbonate.

The ferrite of lime (the name which I have given to this compound) is a light amorphous powder, of a perfectly white colour although it contains 42 per cent. of peroxide of iron; it is insoluble in pure and in sugar-water; boiled with water containing carbonic acid or a soluble carbonate, it is decomposed, and acquires a brick-red colour; the oxide of iron is set free, and mixes with the carbonate of lime. The ferrite of lime may be boiled with caustic potash without experiencing any alteration, which is readily evident from its remaining perfectly white. All acids, even the weakest, decompose the ferrite of lime, and combine simultaneously with the two basic elements.

The composition of the ferrite of lime may be proved in several ways. By dissolving it in hydrochloric acid, it forms a yellow solution, from which ammonia precipitates the whole of the iron in the state of hydrated sesquioxide, which is calcined. The filtered liquid gives with oxalate of ammonia a precipitate of oxalate of lime, which is converted into sulphate. The analysis thus made of a ferrite obtained with an excess of lime, and washed, constantly furnished 4 equivs. of lime to 1 equiv. peroxide of iron. It is probable that the precipitate contains water of combination; but as it is impossible to dry it completely without partly decomposing it, I confined myself to the determination of the respective relation of the two oxides. I moreover ascertained that this double oxide, well washed, contained no potash; by decomposing it entirely with carbonic acid, washing it with boiling water, and evaporating it to dryness, the residue of the evaporation was almost null, and furnished no precipitate with a concentrated solution of bichloride of platinum. When 1 equiv. perchloride of iron, diluted with water and mixed with 4 equivs. chloride of calcium, is precipitated by potash, the precipitate becomes perfectly white in the course of some hours; whilst if only 3 equivs., $3\frac{1}{2}$ or $3\frac{3}{4}$ of chloride of calcium are added to the solution, the precipitate remains coloured although set aside for several months. This last experiment alone would suffice to show that the ferrite of lime considered anhydrous is represented by the formula $Fe^2 O^3, 4CaO$, which corresponds to the per-centage composition—

Peroxide of iron	41·66	1000
Lime	58·34	1400

Independently of its great instability, the ferrite of lime is remarkable from its snow-white colour, notwithstanding that it contains half its weight of peroxide of iron.

Lime and Oxide of Chromium.—When an excess of caustic potash is poured into a solution consisting of a mixture of 1 equiv.

chrome-alum, and of 2, 3, 4, &c. equivs. of chloride of calcium, a green precipitate falls, while the supernatant liquid becomes colourless. As the pure hydrate of the sesquioxide of chrome dissolves in a cold solution of potash, forming a green liquid, the preceding experiment led me to suppose the formation of a compound of lime and sesquioxide of chrome.

The precipitates containing more than 2 equivs. of lime to 1 of sesquioxide of chrome part with the excess of lime to sugar-water, so that the compound $Cr^2O^3, 2CaO$ is always obtained.

The same compound is produced in a still more simple manner, by substituting ammonia for the potash; in this case the excess of lime, instead of being precipitated, remains in solution in the ammonia. The well-washed precipitate, treated with dilute sulphuric acid and then mixed with alcohol, furnishes a white precipitate of sulphate of lime; whilst the liquid and the wash-waters deposit, under the influence of ammonia, all the sesquioxide of chrome they contained. Several analyses of the double oxide led to the formula $Cr^2O^3, 2CaO$, which requires 57·75 Cr^2O^3 and 42·25 CaO.

The chromite of lime forms a slightly-gelatinous green precipitate, which is tasteless, insoluble in pure water, ammonia and in potash; it is less easily and far more slowly decomposed by free carbonic acid or the carbonates than the ferrite of lime; but yet it cannot be dried without experiencing decomposition. When heated exposed to the air, it is converted into chromate of lime. The following equation explains this reaction:—

$$Cr^2O^3, 2CaO + O^3 = 2(CrO^3, CaO).$$

The absorption of oxygen takes place at a moderate temperature, far below a dull red heat. I have several times confirmed this fact by heating the chromite of lime in a furnace; the change is easily detected by treating the compound with hydrochloric acid, when chlorine is liberated as with the chromates. The chromite of lime, calcined in an open tube over a spirit-lamp, also yields chromate of lime; but the greater portion of the sesquioxide of chrome separates in the form of a green crystalline powder.

The formation of this compound shows clearly how inaccurate a result would be obtained in analysis by precipitating chrome with an alkali, either with or without the assistance of heat, in the presence of a salt of lime. I have stated that the compound of sesquioxide of chrome and lime is insoluble in a cold solution of potash; but when the proportion of lime is less than 2 equivs., the potash redissolves not only the oxide of chrome, but also the lime; thus we obtain with potash a precipitate soluble in an excess with two solutions,—the one formed of 20 parts of chrome-alum and 1 part of marble dissolved in hydrochloric acid; the other of 10 parts of chrome-alum and 1 of marble. The complete precipitation of a mixture of chrome-alum and of chloride of calcium, even in very considerable excess, is very remarkable; it may however be readily explained; the supernatant liquid contains but a trace of lime; the salts of lime, in the presence of an excess of potash, deposit the whole of the lime, which in the preceding experiment simply mixed

with the chromite of lime. This insolubility of lime in an alkaline solution is sufficiently remarkable to deserve the attention of chemists.

When 1 part of caustic potash or soda is boiled with 100 parts of water, and an excess, it matters not how great, of hydrate of lime, the filtered liquid, either hot or cold, does not retain more than $\frac{1}{50,000}$th of lime. Although the balance is not capable of determining so small a trace of lime, it is not the less certain that the preceding numbers form a maximum rather than a minimum; for oxalate of ammonia forms, in a solution containing 1 part of lime to 50,000 parts water, a decidedly larger precipitate than in the preceding case. From this experiment it results, that potash and soda can never occur mixed with lime, either in the solid state or in a very weak solution, even when these alkalies have been prepared with a large excess of lime and with the most calcareous waters.

After having ascertained the above facts, I found, as I had expected, that an alkaline solution of potash or soda containing no carbonic acid produced a copious precipitate in lime-water even when highly diluted. This precipitate, which resembles in appearance that produced by carbonic acid, appears to be pure lime. Its formation is owing simply to its insolubility in an alkaline liquid. It follows, as a consequence of this insolubility, that when lime-water is poured into the solution obtained by the action of slaked lime upon the carbonates of potash or soda, in order to ascertain the degree of causticity of these alkalies, there ought always to be, and indeed there is always formed, a white precipitate; so that the complete causticity of the potash and soda cannot be indicated, as has been erroneously pretended, by the absence of a precipitate, and other tests must be had recourse to for the purpose.

I examined whether ammonia possessed, like potash and soda, the property of rendering lime insoluble; since ammonia is frequently employed in analytical investigations, and it presents certain inconveniences when carbonated, it was important to ascertain whether slaked lime would remove the carbonic acid from it without entering into solution. When hydrate of lime is shaken with liquid ammonia containing carbonate, the carbonic acid is entirely removed, but a portion of the lime is held in solution by the ammonia. I mention this reaction, because there are cases in analysis where carbonic acid has to be separated from ammonia, whilst the presence of a small quantity of lime would not interfere with the result.

Lime and Alumina.—Lime combines with alumina under the same conditions as the oxides of iron and chrome. When 2 parts of alum are dissolved in water, and an aqueous solution of 10 parts of potash added, chloride of calcium forms in the liquid a white gelatinous precipitate of aluminate of lime, which retains the whole of the alumina. However alkaline the liquid, not a trace of alumina can be detected in it; this only appears when the mixture is submitted to the action of heat.

Lime and Phosphoric Acid.—The combination of lime and phosphoric acid is formed when chloride of calcium is poured into a

mixture of phosphate of soda and caustic potash; the liquid retains not the slightest trace of phosphoric acid.

Lime and Silica.—Lime combines with silica, forming a white insoluble precipitate, which is obtained by pouring chloride of calcium into an excess of caustic potash mixed with silicate of potash; the liquid contains not a trace of silica, for when saturated by an acid and evaporated to dryness, the residue was entirely soluble in water.

Lime, Alumina and Silica.—When a mixture of alum and of alkaline silicate in an excess of caustic potash is treated with a solution of chloride of calcium, a copious precipitate is formed, which contains silica, alumina and lime; the supernatant liquid, supersaturated with nitric acid, gives no precipitate with ammonia, and contains therefore no alumina. Evaporated to dryness with an excess of acid and dried at 392°, the residue dissolves entirely in acidulated water, proving likewise the absence of silica. In this experiment there is therefore precipitated a substance composed of the same elements as felspar with lime base. As the formation of lime felspar by the humid way has never been examined, and may possess great interest in a geological point of view, it is my intention to examine this compound, and to see whether it be really identical with felspar. —*Comptes Rendus*, July 21, 1851.

On a new Compound of Mercury. *By* MM. Sobrero *and* Selmi.

When a solution is formed of bichloride of mercury in alcohol of 0·828, and the oxide is precipitated by an alcoholic solution of potash, so as to render the liquid strongly alkaline, a yellow precipitate is obtained, which is not oxide of mercury, but a combination of mercury with carbon, hydrogen and oxygen. This precipitate is amorphous and insoluble in water and alcohol; it is freed by washing from the excess of potash and chloride of potassium. In the preparation of this substance, it is advisable to operate at a temperature of about 122° F. This compound is stable at the ordinary temperature; it resists without decomposition a temperature, which we have not ascertained, but which appears to be near 392° F.; heated more strongly, it acquires a slight orange tint, then decomposes suddenly with a violent detonation, being wholly resolved into gaseous products without residue. To obtain this compound furnished with the property of detonating in the manner described, the precipitation should be made under the conditions above mentioned. If the solutions were cold, or if sufficient potash had not been employed, the precipitates obtained are less detonating, and leave a residue of oxide of mercury. By exposure to direct light, the substance quickly turns black. When heated while still moist in a glass tube, it is decomposed with less violence, and yields metallic mercury, water and acetic acid.

In hydrochloric acid this substance dissolves entirely even in the cold; it yields in this decomposition a volatile substance of a peculiar irritating odour, which affects the throat like prussic acid. This

substance may be isolated by distilling the mixture, when it is obtained mixed with hydrochloric acid; we have not yet ascertained its composition, but we have observed that when nitrate of silver is mixed with it, there is obtained, besides the precipitate of chloride of silver, a soluble compound, which crystallizes in very beautiful transparent crystals. Sulphuric acid dissolves the mercurial compound, and furnishes crystalline compounds. Nitric acid likewise dissolves it; the solution yields with caustic potash an ash-gray precipitate, which, on treatment with hydrochloric acid, gives a volatile product having the same odour as that above mentioned. Acetic acid dissolves it almost entirely; the solution furnishes a crystalline substance on evaporation. When boiled with a solution of chloride of ammonium, it expels the ammonia, and at the same time a soluble crystalline compound is obtained. A crystalline compound is likewise procured by boiling the substance with a solution of bichloride of mercury.

Although we have not been able to ascertain the composition of this singular substance, we are able to state that it contains mercury, oxygen, carbon and hydrogen, and that the latter elements are no longer in the same relation as in alcohol, but that the hydrogen is in a far less proportion; that this substance behaves like a strong base, and that it combines not only with sulphuric, nitric and acetic acids, but with several others.

In our investigations, and by varying the reaction in different ways, we have also procured compounds of mercury, which must be related to the above substance. Thus a substance which differs from that above described is formed by pouring slowly a very weak solution of potash into a boiling solution of bichloride of mercury, &c. When mercury is dissolved in nitric acid, and all the nitrous products are expelled by long ebullition, and this solution is mixed with alcohol of 0·848 in the proportions adopted for the preparation of the fulminate of mercury, there is no immediate reaction provided the mixture is made below 212°; but if the mixture is heated to 212°, a white crystalline compound is immediately seen to separate, the formation of which does not stop even when the heat is removed. This reaction, quick as it is, is not accompanied by any disengagement of gas. The precipitate contains oxide of mercury, nitric acid, carbon and hydrogen; when treated with hydrochloric acid, it yields a volatile substance having the peculiar odour above mentioned.

It is probable that, by reactions similar to those we have described, analogous compounds will be obtained by substituting the amylic and æthylic alcohols, &c. for ordinary alcohol, and other metals, such as silver, for mercury.—*Comptes Rendus*, July 21, 1851.

On the Behaviour of Sulphurous Acid towards some Persalts of Copper. *By* O. Dœpping.

The author describes the deportment of sulphurous acid towards the nitrate, acetate and sulphate of copper. In the very dilute solu-

tion of nitrate of copper the acid produced no change. What is stated with respect to the other two salts contains nothing more than is known from the researches of Chevreul, Berthier, Vögel, Rammelsberg and Muspratt. The red crystals which sulphurous acid precipitates from the solution of pernitrate of copper, and those which are subsequently obtained by saturating with carbonate of soda, the author regards as a new sulphite of the protoxide of copper, $3Cu^2O+4SO^2+4HO$.

The red crystals may be washed with water, in which they are insoluble, have neither in the moist nor in the dry state any odour, and do not alter in appearance on desiccation. In hydrochloric acid they dissolve with a yellow colour, with evolution of sulphurous acid; and on the addition of water, protochloride of copper separates if too much hydrochloric acid has not been added. Chloride of barium produces no precipitate in this hydrochloric solution; solution of potash throws down a dirty yellow precipitate.

The crystals dissolve in very dilute nitric acid, without any disengagement of gas, into a colourless liquid, in which no precipitate is formed by a solution of baryta. Strong nitric acid alters them; they dissolve with a blue colour; and solution of baryta now produces in the solution a precipitate which is insoluble in water and acids.

Sulphuric acid expels sulphurous acid, and the crystals change their form and colour. Ammonia dissolves the crystals readily and instantly, with an intense blue colour. Boiled with water, the salt is but slightly affected; on cooling, a yellow coating is deposited on the sides of the vessel; and chloride of barium produces in the liquid a white precipitate, insoluble in hydrochloric acid. No evolution of sulphurous acid is perceptible on ebullition. Dried at 212° in the water-bath, 2·358 grms. of the air-dried salt lost 0·003, and in a second experiment 2·878 lost 0·004 grm. water—a loss which can only be ascribed to hygroscopic water. The salt is not anhydrous; when heated in a test-tube over a spirit-lamp, there is a copious condensation of water on the sides of the tube, and at the same time the odour of sulphurous acid is disengaged. On analysis, the author found—

Cu^2O	55·98	3 =	2673·60	56·55
SO^2	33·23	4	1603·00	33·92
HO	10·68	4	449·92	9·73

If we calculate the author's results according to the formula of the salt recently described by Rammelsberg, $CuO, SO^2+Cu^2O, SO^2+2HO$, we have—

	Found.			
Cu	49·76	3 =	96	49·5
SO^3	33·23	2	64	32·9
HO	10·68	2	18	9·2

This composition agrees therefore with that calculated with Rammelsberg's formula, according to which the red salt contains likewise peroxide of copper. The behaviour towards ammonia corroborates this view.—*Bulletin de St. Pétersbourg*, ix. p. 179.

On the Sulphites of Copper. By M. Rogojski.

Several chemists have examined these salts without being able to agree as to their constitution. The nature of the red sulphite of copper described by M. Chevreul has especially given rise to a difference of opinion; and the analyses made of this substance exhibit, as regards the copper, differences amounting sometimes to 10 per cent. My experiments explain this disagreement in a satisfactory manner, by showing that two red compounds, the composition and reactions of which are entirely distinct, have been taken for identical salts.

When sulphurous acid gas is passed into water holding oxide of copper in suspension, there is not obtained, as admitted by M. Chevreul, a sulphite of the protoxide of copper; but the product, which is well defined and crystallized, constitutes a sulphite of the cuprosocupric oxide, $CuO, SO^2 + Cu^2 O\ SO^2 + Aq$.

This composition is verified by the reaction of hydrochloric acid, which immediately converts it into a mixture of the white protochloride and the green perchloride of copper.

When this sulphite of the protoperoxide of copper is dissolved in ammonia, and the solution, which is of a deep blue colour, is exposed to the action of sulphurous acid gas, it is decolorized, and deposits a beautiful white salt crystallized in little spangles, which is a new sulphite, having copper and ammonia for base, $CuO, SO^2 + NH^4 O, SO^2$. This immediately furnishes, on being mixed with the solution of persulphate of copper, the red salt of M. Chevreul, which again proves that it is not a sulphite of the protoxide of copper.

I have succeeded, by a very simple process, in producing the true protosulphite of copper; it consists in passing an excess of sulphurous acid gas into water holding in suspension my sulphite of ammonia and protoxide of copper; this is immediately converted into a minimum red crystalline powder, which contains $2(Cu^2 O, SO^2 + Aq$. With hydrochloric acid this salt yields only white protochloride of copper.

The sulphite of soda, and especially the sulphite of ammonia, may likewise be employed for the preparation of the sulphite of the protoperoxide of copper; but the sulphite of potash furnishes a product which always contains a constant amount of potash in the relation $KO, SO^2 + CuO, SO^2 + Cu^2 O, SO^2$.—*Comptes Rendus*, June 30, 1850.

On certain Salts and Products of Decomposition of Comenic Acid. By Mr. Henry How*.

Comenic acid was discovered by Robiquet†, who observed that meconic acid undergoes a change of properties when boiled with water, carbonic acid being evolved, and a product obtained to which he gave the name *parameconic acid*, indicative of isomerism with the original substance. Liebig‡ however pointed out that there was

* From the Transactions of the Royal Society of Edinburgh, vol. xx. part 2; having been read before the Society April 7, 1851.

† Ann. de Chim. et de Phys., vol. li. p. 244. ‡ *Ibid.*, vol. liv. p. 26.

also difference in composition, and proposed the provisional name *metameconic acid* for the new substance, whose composition he represented by the formula $C^{12} H^4 O^{10}$, derived from the analysis of the acid itself and of a silver salt. In a subsequent paper* he showed its bibasic nature, and entered fully into the relations between it, which was now named *comenic acid*, *meconic acid* and *pyromeconic acid*, the product of dry distillation common to both the former bodies. The subject was further discussed by Dr. Stenhouse†.

I employed for the preparation of comenic acid the process of Robiquet as modified by Gregory, which consists in boiling crude meconate of lime (or, still better, the acid salt obtained by once treating this substance with boiling water and hydrochloric acid) with a quantity of pretty concentrated hydrochloric acid sufficient to dissolve it. For the purification of the acid, which is deposited in the form of very dark-coloured, hard, crystalline grains, Stenhouse recommends solution in a slight excess of caustic potash or soda, and recrystallization of the salt deposited from the boiling fluid. I preferred however to use ammonia, since, if certain precautions are adopted, a salt is obtained as readily deprived of colour as the potash salt, and much more insoluble in cold water than the corresponding salt of soda; while the mother-liquors afforded a convenient means of trying the action of various chemical agents upon the acid. The process I employed consists in boiling the dark-coloured grains in water, with gradual addition of caustic ammonia, till the whole is in solution. The fluid is then immediately filtered. The addition of an excess of ammonia and the continuance of a boiling heat are to be avoided, as there ensues, if this be not attended to, a curious decomposition, attended with the production of much colouring matter, the explanation of which will be entered into subsequently.

The ammonia salt obtained as above deposits from the black fluid in yellow hard crystals if the solution is left at rest, but in soft silky prisms when it is agitated; in the latter state the salt is not so readily washed free of the coloured mother-liquor. By two or three crystallizations from boiling water, a salt of dazzling whiteness, in fine radiated four-sided prisms, is obtained.

From solutions of this salt, which, when even quite pure, have a faint shade of straw colour, the addition of concentrated hydrochloric acid throws down comenic acid in the form of a white heavy crystalline powder adhering to the sides of the vessel, which, when dissolved in boiling water, in which it is not very soluble, is deposited from a saturated solution in grains and crusts, almost colourless; but as the solution cools, groups of short, prismatic, or sometimes leaf-like crystals appear, always possessing a characteristic yellowish-red tinge of colour.

Bicomenate of Ammonia.—This salt was obtained and analysed by Stenhouse, who formed it by solution of the acid in a slight excess of ammonia, and subsequent concentration *in vacuo* over sulphuric acid. He describes it as "partly amorphous, partly crystalline;" he found that it lost 2 equivs. of water on drying at 212°.

* Ann. der Chem. und Pharm., vol. xxvi. † Mem. and Proc. Chem. Soc., vol. i.

As obtained by the process above given, it is in the form of square prismatic crystals, white and of great brilliancy, presenting when in mass a beautiful appearance. It is very soluble in boiling water, very little soluble in alcohol. It has a strong acid reaction; and is deposited, even from a solution of the acid, in an excess of hot caustic ammonia, if the boiling has not been continued. It is represented by the formula $NH^4O, HO, C^{12}H^2O^8 + 2Aq$.

My own analyses agree with this, which is the result of the analyses of Dr. Stenhouse; but a salt containing an additional single atom of water is obtained when strong alcohol is added to cold saturated alkaline solution of comenic acid in ammonia. It falls in groups of radiated prisms. The air-dried salt lost at 212° F. 13·73 per cent. of water; the formula $NH^4O, HO, C^{12}H^2O^8 + 3Aq$ requires 13·50.

Bicomenate of ammonia, in the dry state, sustains a temperature of 350° F. without decomposition or loss of weight. When heated to 390° F. in a closed tube, it blackens and fuses; and on examination it is found to have undergone a change, an acid substance being produced, which I shall describe fully hereafter.

Bicomenate of Potash.—When comenic acid is boiled with a slight excess of caustic potash, it dissolves readily, and the fluid on cooling deposits a salt, which, when washed with cold water and subsequently recrystallized from the same menstruum boiling, presents itself in groups of short, square, prismatic needles. They are not very readily deprived entirely of colour. They have a strongly acid reaction, and are the anhydrous bicomenate of potash. They gave the following results on analysis:—

Carbon	37·07	12 =	72	37·07
Hydrogen	1·75	3	3	1·54
Oxygen	..	9	72	37·09
Potash.....	23·88	1	47·2	24·30

The formula is therefore $KO, HO, C^{12}H^2O^8$.

Bicomenate of Soda.—Comenic acid was dissolved in a tolerably strong solution of caustic soda by boiling; the fluid on cooling deposited two forms of crystals, one in mammillated masses, the other in transparent prisms half an inch in length. On washing the mixture with a little cold, and resolution in boiling water, no deposit was obtained on cooling, even after the lapse of some hours; but on evaporation of the fluid to about two-thirds of its bulk, groups of mammillary crystals appeared, which when magnified were found to consist of four-sided elongated prisms. From this it appears that the salt is much more soluble than either the potash or ammonia salt, and cannot be employed with advantage in the preparation of comenic acid. It has an acid reaction, and is anhydrous. It furnished 17·09 per cent. of soda; the formula $NaO, HO, C^{12}H^2O^8$ requires 17·41.

It is obvious, from the foregoing experiments, that neutral salts of comenic acid with the fixed alkalies or with ammonia do not exist in the dry state. That this is not the case with reference to the alkaline earths, I shall now proceed to show.

Salts of Lime with Comenic Acid.

Finely-powdered comenic acid, mixed with water and an excess of carbonate of lime, decomposes the earthy salt with effervescence in the cold. When the liquid is boiled for some time, then filtered and allowed to stand, a few rhombic crystals appear; but by far the larger proportion of the acid remains on the filter in combination with the lime, mixed with the excess of carbonate employed. The crystals were in very small quantity. They consisted doubtless of the acid salt, which I obtained more conveniently in another way.

Bicomenate of Lime.—When a cold, saturated, aqueous solution of bicomenate of ammonia is added to a solution of chloride of calcium, brilliant crystals soon begin to appear, which gradually increase in quantity. They are, though small, perfectly-defined transparent rhombs; they dissolve readily in boiling water, and are deposited on cooling of a larger size than when first obtained. In the following analysis the substance was dried at 250° F., as it was found that the whole water of crystallization was not expelled at 212°, or only after the lapse of a very long time. The lime was determined as sulphate by ignition with a few drops of sulphuric acid, as the salt swelled up inconveniently when heated by itself:—

Carbon	40·83	12 =	72	41·14
Hydrogen	1·94	3	3	1·71
Oxygen	..	9	72	41·15
Lime	16·02	1	28	16·00

Hence the composition of the salt, dried at 250°, is represented by the formula $CaO\,HO, C^{12} H^2 O^8$. The air-dried crystals lost at 250° 26·37–25·92 water of crystallization; the formula $CaO, HO, C^{12} H^2 O^8 + 7Aq$ requires 26·47.

Neutral Comenate of Lime.—This salt is obtained in the form of crystalline grains when a solution of the acid ammonia salt, to which an excess of ammonia has been added, is poured into a solution of chloride of calcium. According to the state of dilution of the fluids employed, salts containing different amounts of water of crystallization are obtained, and the appearance of the product varies accordingly. They are all insoluble in water. The well-washed substance gave the following results, the lime being estimated as sulphate, because the salt when dried blows up in a cloud on ignition:—

Carbon	34·20	12 =	72	33·96
Hydrogen	2·36	4	4	1·88
Oxygen	..	10	80	27·75
Lime	26·59	2	56	26·41

The formula of the salt, dried at 250°, is therefore $2CaO, C^{12} H^2 O^8 + 2HO$, 2 equivs. of water being retained at this temperature.

As before mentioned, salts containing various amounts of water of crystallization are formed in more or less concentrated solutions. The crystals of that one whose analysis in the dry state is given were in the form of groups of minute prisms. They were deposited in a tolerably dilute fluid, and lost 5 atoms of water in drying

$=18{\cdot}20 : 17{\cdot}50$, being that corresponding to the formula $2CaO, C^{12} H^2 O^8, 2HO + 5Aq$.

By employing very dilute solutions, a salt was got in very well-defined, small, brilliant crystals, which lost at 250° F. 31·27 per cent. of water; now the number 31·82 is that required by the formula $2CaO, C^{12} H^2 O^8, 2HO + 11Aq$. This dried salt gave 26·35 per cent. of lime, which agrees perfectly well with the results obtained in the former case.

All these neutral salts are converted into basic compounds by simple ebullition in water.

Salts of Baryta with Comenic Acid.

Carbonate of baryta is partially decomposed by comenic acid in the cold, and completely so when heated with an excess in water, the acid comenate of baryta being produced. On the other hand, when a mixture of the acid and an excess of carbonate of baryta is boiled with water, effervescence ensues; but the comenic acid remains undissolved, being in combination with the earth in form of a basic salt. I readily obtained both an acid and a neutral salt by double decomposition.

Bicomenate of Baryta.—A cold saturated aqueous solution of bicomenate of ammonia gives, with a solution of chloride of barium, an immediate precipitate of a crystalline nature. With more dilute solutions the salt appears more slowly in well-defined transparent rhombs. It is readily soluble in boiling water, and has a strong acid reaction. It loses its water of crystallization at 212°, but very slowly; the dried salt fuses on ignition:—

Carbon	31·89	12 =	72	32·19
Hydrogen	1·71	3	3	1·34
Oxygen	..	9	72	32·21
Baryta.....	33·81	1	76·64	34·26

Hence the composition of the salt, dried at 212°, is expressed by the formula $BaO\ HO\ C^{12} H^2 O^8$.

In the crystals 2 equivs. of this substance are combined with 13 of water, viz. 20·95–20·78, which agrees well with the number 20·73, required by the formula $2(BaO, HO, C^{12} H^2 O^8) + 13Aq$.

Neutral Comenate of Baryta.—An alkaline ammoniacal solution of comenic acid causes an immediate precipitate in chloride of barium of minute radiated crystals. In dilute solutions these do not appear immediately, but in a very short time they commence forming, and their quantity increases till the whole fluid is filled. Under these circumstances they present a very beautiful appearance, being in individual groups, whose silky needles radiate regularly from a centre. Under the microscope these needles are seen to be square prismatic crystals.

This salt is insoluble in boiling water, and does not lose its water of crystallization at a temperature of 212°. When dried at 250°, it is almost pyrophoric on ignition, exploding in a light fiery cloud;

for this reason the base was determined as sulphate in the analysis which follows, by ignition with a little sulphuric acid:—

Carbon	23·07	12 =	72	23·27
Hydrogen	1·47	4	4	1·29
Oxygen	..	10	80	25·89
Baryta.....	49·54	2	153·28	49·55

From the above it appears that this salt, like the corresponding one of lime, retains 2 equivs. of water at this temperature, its formula being $2BaO, C^{12} H^2 O^8 + 2HO$. The crystals contain in addition 8 atoms of water = 19·29–18·77, which agrees perfectly with the number 18·88 corresponding to the formula $2BaO, C^{12} H^2 O^8, 2HO + 8Aq$.

The crystallized salt, when boiled in water, is converted into a basic compound, which loses no water at a temperature of 250°. A portion which had been so dried gave on analysis 54·5 per cent. of baryta; this is considerably more than would correspond with a normal neutral salt entirely free from water.

Salts of Magnesia with Comenic Acid.

Acid Comenate of Magnesia.—This salt is much more soluble than the corresponding salts of lime and baryta; it crystallizes out, after some time, in perfect small rhombs, when strong cold solutions of bicomenate of ammonia and sulphate of magnesia are mixed. When obtained from dilute solutions, by spontaneous or very slow artificial evaporation, these crystals are of very large size; and when possessing the yellow colour so apt to adhere to salts of comenic acid, they very much resemble regular crystals of ferrocyanide of potassium. They are readily soluble in hot water, and react strongly acid. The following is the analysis, the magnesia being estimated as sulphate, by ignition with sulphuric acid:—

Carbon	38·62	12 =	72	38·77
Hydrogen	2·97	5	5	2·69
Oxygen	..	11	88	47·41
Magnesia	11·10	1	20·67	11·13

from which it appears that 2 atoms of water are retained in combination at the temperature of 240° F., the composition of the so-dried salt being expressed by the formula $MgO, HO, C^{12} H^2 O^8 + 2HO$. The crystals contain further 6 atoms of water (22·08); the formula $MgO, HO, C^{12} H^2 O^8, 2HO + 6Aq$ requires 22·53.

Neutral Comenate of Magnesia.—When an alkaline ammoniacal solution of comenic acid is added to a solution of sulphate of magnesia, a salt is precipitated, especially on stirring the fluid, in the form of hard crystalline grains, adhering very much to the sides and bottom of the vessel. Under the microscope, those grains are found to be made up of groups of short prismatic needles. They are insoluble in boiling water. They lose their water of crystallization at 212°, but only after long exposure to that heat; thus dried, they give the following results on analysis:—

Carbon	35·07	12 =	72	34·89
Hydrogen	2·53	5	5	2·42
Oxygen	..	11	88	42·66
Magnesia	19·53	2	41·34	20·03

from which it appears that the formula expressing the composition of the salt, dried at 212°, is $2MgO, C^{12} H^2 O^8 + 3HO$.

I endeavoured, by employing a higher temperature, to obtain a salt corresponding with the neutral salts of lime and baryta in the amount of water retained at the same heat; but in the experiment I made, the substance lost weight at 250° gradually through a space of four days, and then the loss between each weighing was very small. It yielded 21·3 per cent. of magnesia, which is more by a half per cent. than is required by a salt of the constitution sought for. The neutral comenate of magnesia, precipitated as above mentioned, has the composition expressed by the formula $2MgO, C^{12}H^2O^8$, $3HO + 8Aq$, the 8 atoms Aq (26·50) being lost at 212°. The number calculated from the above formula is 25·86.

The salts of strontian somewhat resemble in appearance those of baryta, but are more soluble.

It is curious that this acid does not form an acid salt with oxide of copper, the salt with 2 equivs. of base being obtained both by the addition of comenic acid itself and of acid comenate of ammonia to a solution of sulphate of copper. This salt was analysed by Stenhouse, who also examined some others, the details of which will be found in the paper already referred to.

[To be continued.]

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Ipswich, July 2nd, 1851.

On the Constitution of Salts. *By* Alexander W. Williamson, *Professor of practical Chemistry at University College*.*

There is strong reason for believing that all questions concerning the chemical constitution of matter will be most tangible when considered from the point of view of the constitution of salts, which are the groups whose arrangement and transformations are most susceptible of being ascertained experimentally. The elementary bodies themselves have been now shown † to obey a certain force of combination between their particles, analogous though generally inferior to that which holds together the constituents of a salt; and any general conclusions which may be established for salts, will

* Communicated by the Author.

† See Mr. Brodie's research "On the Condition of certain Elements at the moment of Chemical Change."

therefore extend to them. Now to have clear and connected notions of any order of phænomena, it is necessary to be able to judge of the various cases belonging to it from the same point of view; or, in other words, to have a uniform standard of comparison. Thus if the value of mechanical forces had to be compared, it would evidently not do to measure the one in pounds and the other in kilogrammes, unless the relative value of these units were known, *i. e.* unless the statement made in the one could be reduced to its equivalent in the other. Such unity has as yet been but little attended to by the majority of chemists; and the different branches of the science remaining disconnected, their efforts were directed to establish details rather than general laws. Thanks to the numerous facts which have been thus established, it is now possible, and even necessary, to do something more. The researches of MM. Laurent and Gerhardt have been mainly directed to this point, and it is well known how fruitful their conclusions have already proved. The following remarks have an intimate connexion with those conclusions, and will hardly be intelligible without a knowledge of them.

We are all agreed that chemistry is concerned with the material process of the transformations and changes which matter undergoes, and that the study of the properties of matter in themselves, as long as they undergo no change, belongs to physics. The chemical formulæ, by which we describe more briefly than by words the transformations supposed known to take place, have as yet answered that purpose very imperfectly, and have presented great irregularity of method; for although generally denoting a certain arrangement of atoms, or at least certain differences of arrangement, they are sometimes used to describe the origin of a compound or its decompositions, without forming any other representation of its actual constitution than what may be contained in such a statement. M. Gerhardt has, in a recent memoir published conjointly with M. Chancel, given considerable development to this latter method; and his so-called synoptic formulæ will, I think, be found very suggestive and useful expressions. But formulæ may be used in an entirely different, and yet perfectly definite manner, and the use of two distinct points of view will perhaps not be unserviceable. They may be used as an actual image of what we rationally suppose to be the arrangement of constituent atoms in a compound, as an orrery is an image of what we conclude to be the arrangement of our planetary system; and decompositions may be actually effected between them by the exchange of a molecule in one group for a molecule in another. Gerhardt's formula for sulphate of soda (if he extends his principles to inorganic chemistry) would be sulphuric acid plus soda minus water. This, no doubt, gives a possible origin of the salt, but by no means a possible decomposition; in other instances the inverse would be the case. But the term sulphate of soda does not mean a body formed in any one particular way; it is equally applicable to the product of the action of sulphuric acid on chloride of sodium, or on carbonate of soda, or even to the product of the action of soda on sulphate of iron. The written name should be made to represent

what we conceive a compound *to be*, and should be such that it might be formed by any one of the various processes by which the compound may be prepared. Sulphate of soda is a physical term, and corresponds to purely physical properties; for the substance described by it does not by itself undergo any change, but only when acted upon by certain foreign substances under suitable circumstances.

When we study a molecule by itself, we study it physically; chemistry considers the *change* effected by its reaction upon another molecule, and has to describe the process by which that change is effected. A chemical decomposition should therefore be represented by the juxtaposition of the formulæ of the reacting substances, and by effecting in these formulæ the change which takes place in the mixture.

The adoption of such a method will of course necessitate the adoption of types, from which, by the replacement of certain elements or molecules, we can deduce the constitution of more and more complex groups. I believe that throughout inorganic chemistry, and for the best-known organic compounds, one single type will be found sufficient; it is that of water, represented as containing 2 atoms of hydrogen to 1 of oxygen, thus $\begin{matrix}H\\H\end{matrix}O$. In many cases a multiple of this formula must be used, and we shall presently see how we thereby get an explanation of the difference between monobasic and bibasic acids, &c.

I will here give a few examples of the application of this universal type to the formulæ of common substances. The experiments of M. Chancel, agreeing in result with my own, have clearly proved that the numerous family designated as hydrated oxides are not formed by the juxtaposition of an atom of water with an atom of metallic oxide, *e. g.* $K^2O + H^2O$, but that the equivalent of the molecule is half of that quantity, namely $\begin{matrix}H\\K\end{matrix}O$; they are not compounds of water, but products of substitution in water. This fact is as applicable to the compound as to the simple radicals; and alcohols, which are truly hydrated oxides, must be considered as products of substitution of the compound radicals, methyle, CH^3; æthyle, C^2H^5; amyle, C^5H^{11}; œnanthyle, C^7H^{15} (Buis), &c. for half the hydrogen of water, $\begin{matrix}H\\(CH^3)\end{matrix}O$, $\begin{matrix}H\\C^2H^5\end{matrix}O$, &c. The anhydrous oxides of metals have both atoms of hydrogen replaced by the metal, as $\begin{matrix}K\\K\end{matrix}O$, in the same way as common æther, and its homologues have æthyle in place of both the atoms of hydrogen.

In extending this mode of notation to salts and compound æthers, we must of course keep carefully in view the capacity of saturation of their acids, writing the monobasic acids as hydrochloric, nitric, acetic, &c. at half their usual equivalents, ClH, NO^3H, $C^2H^4O^2$, but retaining the customary atomic weights of the bibasic acids, as sulphuric, carbonic, oxalic, &c.

As alcohol is truly an acid in its reaction, we must of course consider the potassium-alcohol, $\begin{matrix}C^2H^5\\K\end{matrix}O$, as its salt, though alkaline in its reactions. We only need to replace 2 atoms of hydrogen in the radical of this salt by oxygen, to have a compound of which the saline character is acknowledged, acetate of potash, $\begin{pmatrix}C^2H^3O\\K\end{pmatrix}O$. The most simple manner of representing the rational constitution of this compound is to state that it contains, in lieu of the æthyle of the former salt, an oxygen-æthyle, C^2H^3O, which we may term othyle. If the 2 atoms of hydrogen in water were replaced by this othyle, we should have anhydrous acetic acid, $\begin{pmatrix}C^2H^3O\\C^2H^3O\end{pmatrix}O$. In fact, the so-called anhydrous acids are nothing else than the *æthers* of the hydrated acids.

Again, by replacing the potassium in the æthylate, $\begin{matrix}C^2H^5\\K\end{matrix}O$, by its equivalent of cyanogen (which may be effected by the action of iodide of cyanogen), we obtain a compound of the composition $\begin{matrix}C^2H^5\\(NC)\end{matrix}O$, that is, cyanic æther. It is well known, from Wurtz's elegant researches, that by acting upon this body by hydrate of potash, we obtain carbonate of potash and æthylamine; that is, in the place of carbonic oxide in the cyanate, we get hydrogen, and reciprocally with the hydrate. Now can this exchange be represented more simply than by stating the fact, that, in the following diagram, the hydrogen of the 2 atoms of hydrate of potash changes places with the carbonic oxide of the cyanate:—

$$\begin{matrix}K^2\\(H^2)\end{matrix}O^2 \quad \begin{matrix}C^2H^5\\N\end{matrix}(CO) \qquad = \qquad \begin{matrix}K^2\\CO\end{matrix}O^2 \quad \begin{matrix}C^2H^5\\N\end{matrix}H^2$$

1 atom of carbonic oxide is here equivalent to 2 atoms of hydrogen, and by replacing them, holds together the 2 atoms of hydrate in which they were contained, thus necessarily forming a bibasic compound, $\begin{pmatrix}CO\\K^2\end{pmatrix}O^2$.

If we knew how to form the compound COCl, *i. e.* phosgen, with half as much chlorine, it would be easy, by the reaction of it upon our æthylate of potassium, to prepare oxalic æther (and chloride of potassium). Oxalic æther is therefore alcohol in which the basic hydrogen is replaced by carbonic oxide with twice the equivalent that it possesses in the carbonates; and the best evidence of the truth of this view is afforded by M. Dumas's elegant reaction of ammonia upon the æther, forming the compound of amidogen with carbonic oxide (oxamide), and replacing the carbonic oxide by hydrogen, *reproducing alcohol*:—

$$\left.\begin{matrix}C^2H^5\\(CO)^2\\(H^2)\end{matrix}O^2\ \begin{matrix}\\H^4\\N^2\end{matrix}\right\} = 2\begin{pmatrix}C^2H^5\\H\end{pmatrix}O.$$
$$(CO)^2H^4N^2$$

Sulphurous acid is another radical capable of replacing hydrogen; and the sulphates are thus reduced to our type, being bibasic from the same reason as the carbonates. We have thus for sulphuric acid. $\frac{SO^2}{H^2}O^2$; acid sulphate of potash, $\frac{SO^2}{HK}O^2$; neutral sulphate, $\frac{SO^2}{K^2}O^2$, &c.

There are various reactions, both of formation and decomposition, of sulphates, which bear out this view; for instance, chlorosulphuric acid, SO^2Cl^2, in contact with 2 atoms of water, at once replaces half the hydrogen in both by SO^2, forming $2(ClH)$ and $\frac{SO^2}{H^2}O^2$. And again, the difference of the action of zinc upon sulphuric acid according to the concentration, evolving at one time hydrogen, at another sulphurous acid, affords evidence that the sulphurous acid is contained in a manner similar to the hydrogen.

Nitric acid presents, according to the usual view of its constitution, a singular difference between its behaviour to organic and to inorganic compounds; but this difference is owing merely to the error of that view. We are taught that nitric acid combines directly with mineral bases; but when reacting upon hydrogen compounds, it has a powerful tendency to replace hydrogen by hyponitric acid. Now if hydrogen, in organic compounds without number, be replaceable by hyponitric acid, why should not also the hydrogen in hydrate of potash be so replaceable? The product of that substitution would be no very improbable body, only common nitrate of potash, $\frac{(NO^2)}{K}O^2$.

One more example, and I have done. Chlorine is well known to react upon hydrogen compounds by replacing hydrogen by chlorine, with formation of hydrochloric acid. So it is also when it reacts upon water in presence of bases, $\frac{Cl}{H}O$ (hydrated hypochlorous acid), and ClH being formed. In like manner we have, for the series of oxygen acids of this radical, the formulæ $\frac{(ClO)}{O}O$, chlorous acid; $\frac{(ClO^2)}{H}O$, chloric acid; $\frac{(ClO^3)}{H}O$, perchloric acid.

In order to accomplish what I above alluded to as a desideratum for the explanation of chemical reactions, namely effecting between the formulæ of the reagents the interchange supposed to take place in the mixture, I have fixed the symbols of those atoms which have to change places upon the extremities of a piece of card, so fixed by a pivot to the board that by turning round 180° it reverses the positions of the exchanging atoms.

I would not have brought before the public considerations so purely theoretical as the above, had I not found the conclusions of considerable practical utility in the study of reactions.

In the theory of types, we owe to M. Dumas an idea which has already been the vehicle of many an important discovery in science, and which is undoubtedly destined to receive still more general application.

To prevent misunderstandings, it may be as well to state, that the radicals which I have here so freely used are not supposed to be in their compounds absolutely the same as in the free state. The same remark applies with equal force to metallic bodies, which on entering into combination give off a certain amount of heat, and thus assume different properties. To say that metallic zinc is contained in its sulphate is an expression authorized by usage, but is only strictly true by abstraction from most of the properties of the metal. The material atom, which under certain circumstances possesses the properties which we describe by the word "zinc," is no doubt contained in the sulphate, but with different properties, and in the chloride with properties different from either; so also of the compound radicals.

It is to be hoped that we may soon be able to give an account of the nature of the processes by which these changes of properties are effected; but that task can only be entered upon when we have obtained exact determinations of the relative momentum of atoms in various compounds, the proportion of which to their masses determines their physical and chemical properties.

On the Cause which maintains Bodies in the Spheroidal State, beyond the Sphere of Physico-chemical Activity. By M. Boutigny.

M. Boutigny referred to the experiments first shown at Cambridge, and their extension since, to explain some of the effects of ancient miracles. Alluding to the disputed points in the explanation of his experiments, as to the repulsion of metals and fluids, and whether the effects were really entirely or not to be attributed to the properties of the thin stratum of vapour, Prof. Boutigny proceeded to show by experiment that when platina wire was coiled up in the form of a flat spiral and made hot, and æther or alcohol fluid placed on it, in the spheroidal state the liquid would not pass through between the spaces, while the vapour readily did so.

In the evening, the members of the Chemical Section had the opportunity of seeing M. Boutigny pass his hand through a stream of liquid red-hot iron as it passed from the furnace.—*Athenæum.*

On a new Method of contracting the Fibres of Calico, and of obtaining on the Calico thus prepared Colours of much Brilliancy. By Mr. Mercer.

Mr. Mercer's discovery may be stated in a few words to be this:—A solution of cold but caustic soda acts peculiarly upon cotton fibre, immediately causing it to contract; and although the soda can be readily washed out, yet the fibre has undergone a change, and water will take its place and unite with the fibre. In a practical view, Mr. Mercer considered that the fibre might be considered by this action to have a sort of acid property to unite with soda and then with other bases. The effect of the condensation was said to be one-fifth to one-third of the total volume of cotton employed. Dr. Playfair then showed some proofs of the influence of this new process upon our cotton manufactures; thus, taking a coarse cotton

fabric, and acting upon it by the proper solution of caustic soda, this could be made much finer in appearance; and if the finest calico made in England, known as 180 picks to the web, was thus acted upon, it immediately appeared as fine as 260 picks. Stockings of open weaving were shown, and the condensation process made them appear as of much finer texture. The effect of this alteration of texture was most strikingly shown by colours. The pink cotton-velvet had its tint deepened to an intense degree by the condensation process. Printed calico, especially with colours hitherto applied with little satisfaction, as lilac, had strength and brilliancy, besides thus producing fabrics cheaply finer than can possibly be woven by hand. The effect was shown of patterns being formed by portions of a surface being protected by gum from condensation. Thus patterns of apparently fine work can easily be produced. It was stated that the fabrics by this process have much strength given them, for a string of calico one-half condensed by caustic soda will break by 20 oz., while the unacted-upon string of cotton broke with 13 oz.—*Ibid.*

On Gambogic Acid and the Gambogiates, and their use in Artistic Painting. *By* Dr. Scoffern.

The author described the composition of gamboge as a gum-resin, and stated that some years since he had proposed the use of a preparation of it for oil-painting. For this purpose he had employed methods to get rid of the gum. To obtain the gambogic acid, he recommended æther to be employed when the colouring matter is dissolved, and by distillation the æther is given off; the last portions however are retained with so much force that a temperature of 230° or 240° obtained, and this would destroy the colour unless water was employed with the æther. About one-twentieth of water was previously added to the ætherial solution of the pigment, or gambogic acid. The gambogiates of lime and other bases were under examination; the gambogiate of iron however produced a rich brown, like asphaltum, but capable of more richness and certainty in oil. From the trials made, the yellow and brown seemed to be permanent colours, having useful properties as oil-colours. He also thought they might be usefully employed in fresco.—*Ibid.*

On Nitro-glycerine and the Products of its Decomposition. *By* Dr. de Vry.

This yellow liquid, nitro-glycerine, seems not to be poisonous; but it explodes at a moderate heat, as was shown by experiment, detonating when the drops of nitro-glycerine on paper were struck a smart blow with a hammer.

From the conversation in the Section, nitro-glycerine appears, like gun-cotton, to have states of apparent inactivity, which are removed by spontaneous causes; for preparations that resist a certain amount of force applied at one time may readily explode soon afterwards.—*Ibid.*

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Action of Heat upon Mellitic Acid. *By* O. L. Erdmann.

It had hitherto been admitted that mellitic acid was sublimed by heat without alteration; such, however, according to the author, is not the case; the sublimate forms a new acid, to which he has given the name of pyromellitic acid.

To prepare this product, mellitic acid is distilled at a gentle heat; the sublimate melts, and runs down the neck of the retort in oily colourless drops, where it solidifies into a radiate white mass; carbon is left in the retort, and the more the greater the heat employed. Simultaneously with the pyromellitic acid, water passes over. The gases produced in this distillation are composed for the greater part of carbonic acid, which is absorbed by an ammoniacal solution of chloride of barium, excepting a small residue, which burns with a blue flame, like carbonic oxide.

As pyromellitic acid is not decomposed by sulphuric acid, it may also be procured by distilling at an increasing temperature a mellitate, for instance of soda or copper, with concentrated sulphuric acid. The product is purified by recrystallization. In this process much carbonic acid, a little carbonic oxide, and towards the end sulphurous acid are evolved. When, towards the end, the retort is heated to redness, it contains only the sulphate nearly free from carbon.

Pyromellitic acid is sparingly soluble in cold, readily soluble in boiling water, so that it can easily be purified by crystallization. To obtain the acid in a state of perfect purity, it suffices to combine it with soda, and to decompose this salt after crystallization from dilute alcohol by hydrochloric or nitric acid. The aqueous solution of the acid strongly reddens litmus, and has a very acid taste. 100 grms. of water at 61° F. dissolve 1·42 of the acid dried at 248°.

From a boiling saturated solution it crystallizes in brilliant rhombic prisms.

Pyromellitic acid is very soluble in alcohol. Concentrated nitric, hydrochloric and sulphuric acids dissolve it on ebullition without decomposing it; water precipitates the sulphuric solution; it may even be evaporated with a mixture of hydrochloric and nitric acids without experiencing any change. It melts by heat, and sublimes at a tolerably high temperature; at the same time however a por-

tion is decomposed, and it leaves a residue of carbon; heated in the air, the melted acid ignites, and burns with a smoky luminous flame. An aqueous solution of the acid precipitates neutral acetate of lead, but not solutions of other salts. With the alkalies it forms crystallizable colourless salts, which are very soluble in water, insoluble in strong alcohol, and sparingly soluble in weak alcohol. The solutions of these salts, especially of the ammonia salt, exhibit the following reactions:—Chloride of barium gives a white precipitate insoluble in boiling water; chloride of calcium gives no precipitate at first in the cold, but subsequently a crystalline deposit separates, which is insoluble in boiling water; it is also formed immediately on ebullition. The sulphate of copper produces no precipitate at first in weak solutions; but when warmed, the mixture becomes turbid, and a crystalline precipitate of pyromellitate of copper is formed; it also separates, without the assistance of heat, after some time, in small green crystals, insoluble in boiling water; concentrated solutions immediately furnish a greenish powder. Acetate of lead gives a bulky, white, crystalline precipitate, insoluble in boiling water; the nitrate of silver, a white crystalline precipitate, nearly insoluble in boiling water; the sulphate of zinc produces no immediate precipitate in the cold, but after some time, and also on the application of heat, a crystalline deposit separates. The perchloride of iron gives a yellowish-brown precipitate; the protosulphate, no precipitate, unless exposed to the air. The sulphates of nickel and cobalt give no precipitate; but on evaporation of the liquid, red or green crystals are obtained. The protosulphate of manganese and the perchloride of mercury cause no change. The protonitrate and the pernitrate of mercury give white precipitates. The chloride of gold produces no change.

To obtain the pyromellitate of silver in a pure state, the author recommends pouring an alkaline pyromellitate into a boiling solution of nitrate of silver in excess.

The atomic weight of the acid, calculated from the silver salt dried at 248° *in vacuo*, was found to be 54·4. It contained 68·01 per cent. oxide of silver. In other experiments the author found 67·64–67·58 per cent. oxide of silver. In all the elementary analyses a small quantity of water was observed; and it was also noticed that this water was formed only on the combustion of the salt. It amounted for 1 equiv. acid to only ½ equiv., viz. 0·32, 0·28 and 0·31 per cent. On this account, and from the pyromellitic acid being formed from an anhydrous acid, it may perhaps be regarded as accidental, in which case the composition of the silver salt would be—

Carbon	17·81	17·73	17·82	
Oxygen	14·18	14·60	14·60	
Oxide of silver	68·01	67·67	67·58	67·7

whence the author deduces the formula $C^5 O^3, AgO$, which requires carbon, 17·7; oxide of silver, 68·2.

A crystalline salt of lime, dried in the air, lost between 248° F. and 266°, 24·6 per cent. of water. The dried salt contained 33·92 per cent. of lime.

The crystallized acid lost at 212°, 12·33 per cent. of water; and in another experiment at 248°, it amounted to 12·53. It furnished on analysis—

	Acid dried.	Acid sublimed.
Carbon	47·27	47·81
Hydrogen	2·34	2·41

The author calculates for the dry acid the formula $C^5 O^3$, HO, which requires C 47·6, H 1·59, and for the crystallized acid $C^5 O^3$, HO + Aq. He explains the formation of the pyromellitic acid by admitting that 2 equivs. of mellitic acid furnish carbonic acid, carbonic oxide and carbon; the latter is oxidized in the treatment with sulphuric acid, and yields sulphurous and carbonic acids. He however observes, that the composition of the lead salt, in connexion with the presence of hydrogen which he observed in the silver salt, might throw some doubt upon the formula above adopted. In fact, a salt of lead, dried at 266°, gave 64·67–64·92 oxide of lead, and some water on calcination. Other determinations gave 65·22, 65·34, 65·23 oxide of lead. A combustion furnished, for the pyromellitate of lead, dried at 392°, carbon 17·55, and hydrogen 0·55. These results have led M. Erdmann to suppose that pyromellitic acid may possibly be $C^{10} HO^6, 2HO$; the silver salt, $C^{10} HO^6, 2AgO$; and the lead salt, $C^{10} HO^6, 2PbO + Aq$; the salt of lime would contain 5 Aq.

The conclusion of the memoir is devoted to some observations relative to the dry distillation of the mellitates. When these salts are calcined in the air, they diffuse an aromatic odour, resembling that of coumarine or of the oil of *Spirea*. The mellitate of copper gives on distillation copious white vapours, which deposit a crystallizable substance and a volatile oil heavier than water, possessing the odour of the oil of bitter almonds; but the quantity of these products is comparatively small.

The crystalline substance is obtained in yellow fusible needles, is nearly inodorous, very soluble in alcohol, sparingly soluble in cold, but readily soluble in boiling water. An analysis made upon 0·184 substance gave—

Carbon	75·14
Hydrogen	3·3

It is probably $C^{28} H^7 O^6$ or $C^{28} H^{12} O^6 = C^{14} H^3 O^3$.

The mellitate of lime furnishes but little vapour.—*Journ. für Prakt. Chem.*, lii. p. 432.

On the Secretion of the Musk Glands of Myogale Moscovitica. *By* Dr. Dœpping.

The fluid which is obtained by pressure from the glands has the consistence of a thick fat oil, a strong odour resembling that of Sumbul-root and musk, produces a fat stain upon paper, has no action upon red or blue test-paper, and does not mix uniformly with water, alcohol or æther.

When the expressed contents of the glands are examined under the microscope with the power of 700, it is seen that vesicles are diffused in the fluid. When the mass is acted upon by strong alcohol or æther, a slight change in the form of the vesicles is perceptible, but no solution of the contents. After evaporation of the æther, a considerable amount of fat remains. Caustic potash saponifies the fat, the vesicles become more distinct and acquire a violet colour, but the vesicular membrane does not appear to be altered by the potash. Ammonia forms with this secretion, as with other fats, an emulsion, in which the unaltered vesicles with their contents, and moreover the much smaller fat globules which are diffused in the ammoniacal liquid, are distinctly seen to float. In proportion as the ammonia volatilizes, the fat globules form again into larger masses.

After the addition of nitric acid, the vesicles contained in the secretion are likewise very distinct; but the membrane appears to have been destroyed and dissolved by the action of the acid, whilst the contents of the cells are prevented from passing into the outer liquid by the enveloping compound produced by the action of the acid on the membrane of the vesicles. This compound forms a violet ring, the colour of which decreases in depth interiorly. Muriatic acid behaves apparently like nitric acid. Acetic acid has no characteristic action on the mass.

When the contents of the glands are submitted to distillation with water, the product possesses the odour of the liquid in a high degree; and a considerable amount of a colourless oil collects upon the distillate, which has neither an acid nor an alkaline reaction.—*Bulletin de St. Pétersbourg*, ix. p. 205.

On the Compound Ureas. *By* A. Wurtz.

Among the series which may be prepared with the compound ammonias, few offer more interest in a theoretical point of view than that which is connected with ordinary urea. The different terms of this series are formed like urea, by the reciprocal action of the elements of cyanic acid and those of an ammoniacal base. If, for instance, methylamine is acted upon by cyanic acid, there is formed, as I have already described, a substance which stands in the same relation to ordinary urea as methylamine to ammonia. It must be viewed as urea in which 1 equiv. hydrogen is replaced by 1 equiv. methyle, C^2H^3; it is methylic urea:—

$$C^4H^6N^2O^2 = C^2\left\{\begin{matrix}(H^4)\\C^2H^3\end{matrix}\right\}N^2O^2.$$

It is prepared by evaporating solutions of sulphate of methylamine and cyanate of potash to dryness, and exhausting the residue with alcohol. The cyanate of methylamine, which is formed by double decomposition, experiences by the action of heat a similar metamorphosis to that which the cyanate of ammonia undergoes; it is converted into a true urea, which differs from ordinary urea by the elements C^2H^2.

Nothing would be more easy than to substitute another ammonia

for methylamine, and to prepare by this method a series of bodies analogous to urea in their constitution and properties. It is however more advantageous to employ a different process, which I described some years ago, to obtain these bodies, and which consists in substituting for cyanic acid the cyanic æthers, which are treated directly with the ammonia. Not only ordinary ammonia, but even the compound ammonias and certain volatile alkalies, react with energy on the cyanic æthers. The numerous compounds which may be thus obtained all possess these common characters, of being neutral to turmeric-paper, of combining more or less readily with nitric acid, and under the influence of potash splitting up into carbonic acid and the respective ammonia.

Their composition is represented by the general formula $C^m H^n N^2 O^2$. I call them *compound ureas*, because they must be regarded as ordinary urea in which 1 or several equivalents of hydrogen are replaced by 1 or more compound molecular groups. I shall now briefly describe the properties and composition of those I have already obtained:—

Methylic Urea, $C^4 H^6 N^2 O^2$.—It crystallizes in long perfectly-transparent prisms with four faces; the crystals are deliquescent. Their aqueous solution, perfectly neutral, is precipitated by nitric acid if somewhat concentrated, just like the solution of ordinary urea.

The *nitrate*, $C^4 H^6 N^2 O^2, NHO^6$, is far less soluble in water than methylic urea itself.

Bimethylic Urea.—This substance crystallizes readily, fuses near 207° F., is not altered by exposure to the air, volatilizes without decomposition, and dissolves readily in water and in alcohol. Both in composition and in its chemical and physical properties, it is perfectly identical with the substance which I obtained by treating methylo-cyanic æther by water. Both substances combine with nitric acid, and should be regarded as urea in which 2 equivs. hydrogen are replaced by 2 equivs. methyle; the composition of bimethylic urea is represented, according to my analyses, by the formula $C^6 H^8 N^2 O^2$. Isomeric with æthylic urea, it possesses entirely different properties, as moreover was to be expected from its constitution, which is expressed by the formula

$$C^2 \left\{ \begin{matrix} H^2 \\ (C^2 H^3)^2 \end{matrix} \right\} N^2 O^2.$$

Potash resolves bimethylic urea into carbonic acid and methylamine, as seen by the following formula:—

$$C^6 H^8 N^2 + 2KO + 2HO = 2(CO^2, KO) + 2C^2 H^5 N.$$

The mode of formation of bimethylic urea is expressed by the following formulæ:—

1. $2C^4 H^3 NO^2 + 2HO = 2CO^2 + C^6 H^8 N^2 O^2$.
   Methylocyanic æther. Bimethylic urea.

2. $C^4 H^3 NO^2 + C^2 H^5 N = C^6 H^8 N^2 O^2$.
   Methylocyan. æther. Methylamine. Bimethylic urea.

I combined with nitric acid the bimethylic urea formed under these two circumstances, and obtained in both cases the nitrate $C^6 H^8 N^2 O^2$, NHO^6.

Æthylic Urea, $C^6 H^8 N^2 O^2$, is very soluble in water and in alcohol, and separates from the alcoholic solution in bulky striated prisms. These crystals are decomposed near 390°, giving off ammonia, and furnishing various solid products, which I have separated one from the other. The aqueous solution of æthylic urea is decomposed by chlorine; a very heavy chlorinated liquid is formed, which sometimes solidifies to a crystalline mass by the next day. Nitric acid does not precipitate the aqueous solution; but a crystallized compound of æthylic urea with this acid is readily obtained by evaporating the acid mixture under the air-pump.

Biethylic Urea.—This is the substance which I obtained some time ago by the action of water upon cyanic æther, and which is identical with that procured by treating cyanic æther with æthylamine. These two reactions are represented by the formulæ—

1. $2C^6 H^5 NO^2 + H^2 O^2 = C^2 O^4 + C^{10} H^{12} N^2 O^2$.
2. $C^6 H^5 NO^2 + C^4 H^7 N = C^{10} H^{12} N^2 O^2$.

Cyanic æther. Æthylamine. Biethylic urea.

When the aqueous solution of biethylic urea, obtained by either of these processes, is mixed with nitric acid, and the liquid evaporated on the water-bath, flat rhomboidal prisms of the nitrate of biethylic urea are obtained, which are very acid, highly deliquescent, and contain $C^{10} H^{12} N^2 O^2$, NHO^6.

By treating cyanic æther with methylamine, a highly deliquescent urea, containing $C^8 H^{10} N^2 O^2$; it is methyloethylic urea.

Amylic Urea, $C^{12} H^{14} N^2 O^2$, is formed by the action of ammonia upon amylocyanic æther. I obtained only a small quantity of this urea. It combines with nitric acid, forming a crystallizable compound which is unalterable in the air.

Æthyloamylic urea is obtained by treating cyanic æther with amylamine—

$$\underset{\text{Cyanic æther.}}{C^6 H^5 NO^2} + \underset{\text{Amylamine.}}{C^{10} H^{11} N} = C^2 \left\{ \begin{matrix} H^2 \\ C^4\ H^5 \\ C^{10} H^{11} \end{matrix} \right\} N^2 O^2.$$

Aniline dissolves immediately in cyanic æther, with considerable disengagement of heat; on cooling, the liquid solidifies to a crystalline mass of phenyloethylic urea, $C^{18} N^{12} N^2 O^2$; potash slowly decomposes it into carbonic acid, aniline and æthylamine, as shown by the following equation:—

$$C^{18} H^{12} N^2 O^2 + 2KO + 2HO = 2(CO^2, KO) + C^{12} H^7 N + C^4 H^7 N.$$

Coniine likewise dissolves in cyanic æther, with disengagement of heat, and immediately furnishes a compound urea which congeals to a solid mass on cooling. There is no doubt that picoline, toluidine, and the other volatile alkaloids containing 1 equiv. nitrogen, behave in the same manner. Even nicotine, the equivalent of which is not yet well established, acts, although more slowly, upon cyanic

æther, and produces beautiful plates of a compound which may serve to determine the true constitution of nicotine.

The ureas, whose mode of formation I have described, evidently belong to two different series. In the one should be arranged the compounds derived from ordinary urea, by the substitution for 1 equiv. hydrogen of a compound molecular group; in the other, those which are derived from ordinary urea by the substitution of two compound molecular groups for 2 equivs. hydrogen. These two series comprise the following bodies:—

Methylic urea..	$C^2\left\{\begin{matrix}H^3\\C^2H^3\end{matrix}\right\}N^2O^2$	Bimethylic urea	$C^2\left\{\begin{matrix}H^2\\(C^2H^3)^2\end{matrix}\right\}N^2O^2$
Æthylic urea..	$C^2\left\{\begin{matrix}H^3\\C^4H^5\end{matrix}\right\}N^2O^2$	Biethylic urea	$C^2\left\{\begin{matrix}H^2\\(C^4H^5)^2\end{matrix}\right\}N^2O^2$
Amylic urea..	$C^2\left\{\begin{matrix}H^3\\C^{10}H^{11}\end{matrix}\right\}N^2O^2$	Methyloethylic urea.....	$C^2\left\{\begin{matrix}H^2\\C^2H^3\\C^4H^5\end{matrix}\right\}N^2O^2$
		Æthylamylic urea	$C^2\left\{\begin{matrix}H^2\\C^4H^5\\C^{10}H^{11}\end{matrix}\right\}N^2O^2$
		Phenylethylic urea	$C^2\left\{\begin{matrix}H^2\\C^{12}H^5\\C^4H^5\end{matrix}\right\}N^2O^2$
		Conylethylic urea	$C^2\left\{\begin{matrix}H^2\\C^{16}H^{13}\\C^4H^5\end{matrix}\right\}N^2O^2$

The facility with which the ammonias of the series $N\left\{\begin{matrix}H^2\\C^mH^n\end{matrix}\right\}$ form compound ureas induced me to study the action which the ammonias of M. Hofmann, belonging to the series $N\left\{\begin{matrix}H\\(C^mH^n)^2\end{matrix}\right\}$ and $N(C^mH^n)^3$, exert upon cyanic æther. I therefore treated this æther with biethylamine and triethylamine, in the hope of obtaining the triethylic and quadriethylic ureas. The products formed are more deliquescent, more volatile, and crystallize with greater difficulty than the ureas of the formula $C^2\left\{\begin{matrix}H^2\\(C^mH^n)^3\end{matrix}\right\}N^2O^2$. The analyses which I have hitherto made do not admit of any definite opinion being pronounced.

I have just learned from M. Hofmann, that he has obtained in a direct manner the ureas in question, by combining cyanic acid with triethylamine and the oxide of quadriethylamonium.—*Comptes Rendus*, March 24, 1851.

On Nitrous Acid. *By* Prof. Fritzsche.

On the occasion of some experiments which were made on a large scale during the winter of 1849–50, in St. Petersburgh, for lighting the town by means of galvanic batteries, a large amount of nitric acid was employed, which during its use in the battery had acquired

a dark blue colour. The author distilled and rectified this liquid several times, passed the evolved gases through recipients which were strongly cooled by a mixture of snow and chloride of calcium, and in this manner finally obtained pure nitrous acid of a deep indigo-blue colour, and possessing all the properties which the author observed and described in 1840.—*Bulletin de St. Pétersbourg*, ix. p. 193.

On certain Salts and Products of Decomposition of Comenic Acid. By Mr. Henry How.

[Continued from page 334.]

Products of Decomposition of Comenic Acid.

By Oxidation.—The conversion of comenic into carbonic, oxalic and hydrocyanic acids by the agency of nitric acid was noted among the first facts connected with the subject. It takes place with very dilute acid. When tolerably strong nitric acid is employed, the action is very rapid and violent; and when once commenced by application of a gentle heat, is completed in very few minutes, though the heat be withdrawn.

Dr. Stenhouse, in the paper before mentioned, states that when comenic acid is kept for some hours at a temperature of 150° F. in a solution of persulphate of iron, yellow crystals are formed, which contain protoxide of iron and an acid which is not comenic acid. I did not succeed in obtaining a similar result on a repetition of his experiment, possibly because the circumstances were not strictly the same. I think it possible however that these crystals consisted of oxalate of protoxide of iron, from the ease with which comenic acid is oxidized when boiled in a solution of persulphate of iron. I treated a quantity of comenic acid in this way; effervescence of carbonic acid ensued strongly, and the fluid was found to contain much protoxide of iron and oxalic acid. I identified the latter by a preparation and analysis of its lime-salt in a pure state, after the removal of the iron and sulphuric acid by appropriate means.

I could not succeed in producing any change by the action of sulphurous acid or of sulphide of hydrogen upon comenic acid.

Action of Chlorine on Comenic Acid.

Chlorocomenic Acid.—When a current of moist chlorine is passed through water holding powdered comenic acid in suspension, a portion of the acid is dissolved, and the clear liquid deposits, after a lapse of some time, long, brilliant and colourless prismatic needles of the new acid. The same effect is produced when a solution of the ammonia salt is employed; and as, from the more ready solubility of this substance, results were more conveniently obtained, I used it in preference in my experiments.

If an alkaline ammoniacal solution of comenic acid be exposed to the action of chlorine, the first result is a precipitation of the acid comenate of ammonia; but if a cold, saturated, coloured solution of the latter salt be employed, and the gas be passed through it for

some time, the whole of the colour disappears, or the liquid only retains the faint yellowish-green characteristic of an aqueous solution of chlorine, without the formation of an immediate precipitate. After the lapse of some hours, groups of long, colourless, prismatic needles are deposited, the quantity of which is increased by the addition of hydrochloric acid. The mother-liquor, on gentle evaporation, gradually acquires a brownish shade of colour, which passes ultimately into a very dark brown, and then deposits a further quantity of the new acid in prismatic crystals, separate and in groups, of a brown, nearly black, lustrous appearance. In this second mother-liquor, in addition to the colouring matter, oxalic acid is to be detected. The colourless crystals at first obtained, after washing with cold water, were recrystallized from boiling water, in which they are readily soluble. They acquired, in this process, a slight shade of yellow, and presented themselves in the form of short, thick square prisms. They gave the following results on analysis :—

Carbon	37·53	12 =	72	37·79
Hydrogen	1·79	3	3	1·57
Oxygen	..	10	80	42·01
Chlorine	18·77	1	35·5	18·63

The above shows this substance to be an acid, formed by the substitution of an equivalent of hydrogen in comenic acid by an equivalent of chlorine, according to the following equation :—

$$2HO, C^{12} H^2 O^8 + 2Cl = 2HO, C^{12} \left\{ \begin{matrix} H \\ Cl \end{matrix} \right\} O^8 + HCl.$$

It crystallizes with 3 equivs. of water (12·47 p. c.), which are readily expelled at 212°. The formula $2HO, C^{12} (HCl) O^8 + 3Aq$ requires 12·41.

This acid, as before mentioned, is readily soluble in hot water, less so in cold, but under both circumstances its solubility is much greater than that of the parent acid; it is very soluble in alcohol when warm. It imparts to persalts of iron the same deep red colour as meconic and comenic acids. When a piece of granulated zinc is placed in its aqueous solution, hydrogen is slowly evolved, and both zinc and hydrochloric acid are found in the liquid. Nitric acid rapidly decomposes it, with formation of hydrochloric, hydrocyanic, carbonic and oxalic acids. Submitted to destructive distillation, it fuses and blackens; hydrochloric acid is evolved in large quantity, and towards the end of the process a small quantity of a crystalline sublimate appears. This product I obtained in too small quantity to examine thoroughly. I imagine it however to be pyrocomenic acid, and attribute the presence of the traces of chlorine I detected to the impossibility of completely purifying the little matter I had at my disposal.

Chlorocomenic acid, like comenic acid, is bibasic, forming two series of salts. The salts I chose for controlling the analysis, and establishing the saturating power of the acid, were those of silver.

Bichlorocomenate of Silver.—A warm aqueous solution of the acid gives with nitrate of silver a white precipitate in feathery cry-

stals. When freed from the excess of solution of silver and nitric acid by washing with cold water, in which it is sparingly soluble, it may be recrystallized from boiling water, from which it separates on cooling in brilliant, short, prismatic needles. It is not at all, or very slightly, decomposed by boiling in water when no free nitric acid is present. This salt, dried at 212°, gave on analysis 39·03 per cent. oxide of silver; the formula AgO, HO, C^{12} (HCl) O^8 requires 39·01.

The crystallized salt appears to be a combination of the above with water, in the proportion of 3 equivs. of the latter to 2 of the former. The air-dried salt lost at 212°, 4·22–4·66, the mean of which agrees well enough with the number 4·33, corresponding to the formula 2(AgO, HO, C^{12} HCl O^8) + 3Aq.

Neutral Chlorocomenate of Silver.—This salt is obtained in the form of a yellow, flocky, amorphous substance, on the addition of a solution of the acid in a slight excess of ammonia to nitrate of silver. It is insoluble in boiling water, and acquires in the process of drying, the consistence and adhesiveness of clay, which it also closely resembles in appearance.

Considerable difficulty was experienced in the analysis of the salt, since it cannot be burned, as a portion of the chlorine of the acid remains in combination with the metal upon ignition, and it is moreover insoluble in water. When boiled with hydrochloric acid, a part of it escapes decomposition; and if the attempt be made to dissolve it by aid of nitric acid, and precipitate the silver by hydrochloric acid, care must be taken to prevent the formation of cyanide of silver, which readily takes place when either of the silver salts is kept warm with even dilute nitric acid. I obtained 56·85 per cent. oxide of silver; the formula 2AgO, C^{12} (HCl) O^8 requires 57·37.

The other salts of chlorocomenic acid, as might be anticipated, present close analogies with those of comenic acid; the former are generally more soluble than the latter. I have been unable to prepare neutral salts of the alkalies.

The acid salts of potash, soda and ammonia crystallize readily; a solution of the latter salt gives, with the chlorides of calcium and barium, radiated groups of needles, appearing more or less quickly according to the state of concentration of the fluids; with sulphate of magnesia, a few crystals after some time; with sulphate of copper, a rapidly-appearing crystalline salt. The neutral salts of these bases appear generally to be insoluble amorphous substances.

Action of Bromine on Comenic Acid.

Bromocomenic Acid.—As might be expected, the behaviour of comenic acid towards bromine is closely similar to that which it exhibits when submitted to the influence of chlorine. It dissolves readily in aqueous bromine, yielding a colourless fluid if the bromine is not in great excess. In the course of a few hours the new acid s deposited in fine, square, prismatic crystals, often of considerable length, and presenting a very beautiful appearance, from their high refractive power.

It may also be obtained by the addition of bromine water to solution

of acid comenate of ammonia; but I found it more convenient to employ the acid itself. I may mention that, in one instance, when operating upon a solution of the ammonia salt, a considerable excess of bromine failed to yield any new acid, even after the lapse of many hours. The solution remaining colourless, more bromine was added; and as no crystals appeared, the fluid was evaporated, but still without any signs of bromocomenic acid; and it was not until the liquid was reduced to a very small bulk, that any substance crystallized out. On pouring off the liquid, which had now become nearly black, there were found some considerable-sized transparent crystals, together with a little bromocomenic acid in groups. The crystals became perfectly colourless on washing with a few drops of water; they proved to be oxalic acid. This acid always appears in the mother-liquors from which chloro- and bromocomenic acids have been separated by evaporation, resulting probably from a secondary decomposition.

The crystals, as obtained by the action of bromine water upon comenic acid, after being washed and recrystallized from boiling water, gave the following results:—

Carbon	30·75	12 =	72	30·63
Hydrogen	1·49	3	3	1·27
Oxygen	..	10	80	34·06
Bromine	34·15	1	80	34·04

which show that they consist of an acid precisely analogous to chlorocomenic acid, an equivalent of bromine taking the place of one of hydrogen in the comenic acid. In the hydrated state it contains, like the chlorine acid, 3 atoms of water. The air-dried salt lost at 212°, 10·32 per cent. of water; 10·30 is the number required by the formula $2HO\ C^{12}(HBr)\ O^8 + 3Aq$.

This acid so closely resembles the chlorocomenic in its general properties and products of decomposition, that a very few words will suffice to describe it. It is rather less soluble in hot water and in alcohol than the former acid; it is deposited from alcohol in fine rhombic crystals. It is decomposed by zinc. With nitric acid it gives hydrobromic, hydrocyanic, carbonic and oxalic acids.

The acid ammonia salt crystallizes in fine long needles; the acid salts of potash and soda also crystallize. I could obtain no neutral alkaline salts. The acid salts of the alkaline earths are very soluble; the neutral salts are insoluble and amorphous.

The acid silver salt was obtained by adding a warm aqueous solution of bromocomenic acid to an aqueous solution of nitrate of silver; the flocky precipitate which fell was well washed with cold, and subsequently dissolved in boiling water. This fluid deposited the salt on cooling in brilliant, short, prismatic crystals. It furnished 33·64 oxide of silver; the formula $AgO, HO\ C^{12}(HBr)\ O^8$ requires 33·93.

A neutral silver salt was also obtained as a yellow amorphous precipitate by adding solution of the acid in slight excess of ammonia to nitrate of silver in excess; it presented on drying the clayey character I remarked in the corresponding salt of chlorocomenic

acid. As there could exist but little doubt of its composition, I thought it useless to occupy time with an analysis of it.

Iodine appeared, from some experiments I made, to be without the power of decomposing comenic acid.

Acid Comenic Æther.

Comenovinic Acid.—From the bibasic nature of comenic acid, and a consideration of the fact that Dr. Stenhouse* failed in a special attempt to obtain a neutral æther of this acid, I was led to seek it in its combination with æther, a compound of an acid nature analogous to sulphovinic, tartrovinic, and the other acids similarly constituted. I did not succeed in my endeavour to form such a substance by the action of sulphuric acid on alcohol and comenic acid; but was more successful in a slight modification of the method usually adopted for the production of organic æthers. Comenic acid in the state of fine powder was suspended in absolute alcohol, in which it is insoluble *per se*, and a stream of dry hydrochloric acid gas was passed through the fluid. After some time the whole or the greater part of the acid was taken up, the last portions disappearing very slowly. The clear solution gave no deposit, even on standing at rest for many hours, nor was any precipitate produced by the addition of water; but when it was evaporated to dryness, at a heat somewhat below 212°, a crystalline residue remained, which was evidently not comenic acid. This was kept at the same heat till it ceased to smell of hydrochloric acid; it was then dissolved in water under the boiling-point; the fluid on cooling deposited well-defined, square, prismatic needles of considerable size. A portion, dried *in vacuo*, gave the following results on analysis:—

Carbon	52·07	52·18	16 =	96	52·17
Hydrogen	4·50	4·63	8	8	4·34
Oxygen	..	..	10	80	43·49

From which it will be seen that this substance has the composition of an acid æther, or true vinic acid, and is represented by the formula HO, $C^4 H^5 O$, $C^{12} H^3 O^3$; and I shall presently show that the atom of water is capable of being replaced by bases. The acid crystallizes, like the corresponding compound of tartaric acid, without water.

Comenovinic acid is readily soluble in hot water, and may be boiled a short time without undergoing decomposition; but if long kept at this temperature, comenic acid is reproduced. It is extremely soluble in alcohol. It commences to volatilize, when kept in a dry state, at 212°; it fuses at 275° F. into a transparent brownish liquid, which becomes on cooling a crystalline striated mass. When kept at about its fusing-point, it sublimes, unaltered in composition, in brilliant, long, flattened prisms, of great beauty; the second analysis, above given, is that of the sublimed product. It gives a strongly acid reaction with test-papers; its aqueous solution

* Mem. and Proc. Chem. Soc., vol. i.

readily coagulates the white of eggs; it imparts to persalts of iron a deep red colour.

Though of so stable a nature *per se*, this substance rapidly decomposes in contact with fixed bases, so that I have been unable to obtain any of its salts in the dry state. All those I have attempted to prepare gave upon analysis results closely agreeing with the composition of salts of comenic acid, with which their general properties were also identical, notwithstanding that I carefully avoided application of heat.

I obtained a salt of ammonia by passing the dry gas into a solution of the acid in absolute alcohol. Under these circumstances a precipitate soon forms, in small silky tufts of a yellow colour. They preserve their silky appearance on being dried, but soon commence to lose ammonia in a dry atmosphere. A portion of the substance, which had been exposed one night, was placed *in vacuo* over sulphuric acid; it was found to lose less weight by about half a per cent. than would correspond to the ammonia in a salt of the composition $NH^4O, C^4H^5O, C^{12}H^2O^8$. As the residue was found to consist of pure comenovinic acid, there can be little doubt that the above is a true ammonia salt.

Its other salts, with the alkalies and alkaline earths, are very soluble. Its silver salt is gelatinous, and rapidly decomposable even in the dark.

Decomposition of Comenate of Ammonia.

Comenamic Acid.—I mentioned, in a former part of this paper, that bicomenate of ammonia is decomposed, when subjected to a temperature of 390° F., in a sealed tube. The contents of the tube were a black carbonaceous mass, which partially dissolved in boiling water. The filtered solution gave, with hydrochloric acid, a white scaly precipitate, separating on cooling. I did not endeavour to procure more of this substance in this manner, as I considered it to be comenamic acid, which a more convenient process enabled me to obtain in sufficient quantity.

When a solution of comenate of ammonia, containing an excess of the alkali, is boiled, it soon becomes coloured, and after some little time a black-red fluid is obtained; if the boiling be continued till the whole or the greater part of the excess of ammonia is expelled, and the fluid be then allowed to cool, a gray sediment falls to the bottom of the vessel. This, when thrown upon a filter, is found to have a most peculiar, clayey, tenacious character; it is the ammonia salt of comenamic acid, very impure, from adhering colouring matter. It dissolves, though sparingly, in boiling water; and hydrochloric acid, added in just sufficient quantity to decompose it, precipitates very dark bronze-coloured scales of comenamic acid, which separate completely when the liquid cools. Excess of hydrochloric acid is to be avoided, as the new acid is extremely soluble in this reagent. The dark crystals are readily deprived of their colour by two or three crystallizations from boiling water, and very easily by the aid of animal charcoal, which must however for

this purpose be entirely free from iron, as the least quantity of this substance imparts a purple colour to solutions containing the acid.

When pure, comenamic acid presents itself in the form of brilliant colourless plates; dried at 212°, it gave on analysis:—

Carbon	46·00	46·32	12 =	72	46·45
Hydrogen	3·57	3·41	5	5	3·22
Oxygen	..	..	8	64	41·30
Nitrogen	9·17	..	1	14	9·03

It is obvious that this substance is an acid amide, analogous to oxamic acid, and that its constitution is expressed by the formula of acid comenate of ammonia minus 2 atoms of water = HO, $NH^2 C^{12} H^2 O^7$*.

It crystallizes with 4 equivs. of water. The air-dried acid lost at 212°, 19·07–18·56 per cent. of water; the formula $HO, NH^2 C^{12} H^2 O^7 + 4HO$ requires 18·84.

Comenamic acid, as obtained above, is in brilliant scales, very slightly soluble in cold water; the crystals effloresce, and partially lose their lustre in a dry atmosphere. It is soluble in boiling spirit, but very slightly in absolute alcohol. It has a powerful acid reaction, dissolves readily in excess of alkalies, also with extreme facility in the strong mineral acids. From a solution in any of these, ammonia, added in quantity not quite sufficient to neutralize the whole of the solvent, throws down a granular precipitate of the ammonia salt. Its aqueous solution imparts to salts of peroxide of iron a magnificent and deep pure purple colour, which is destroyed by a few drops of a mineral acid, but reappears on dilution of the fluid with water. It is decomposed by boiling with caustic potash, with evolution of ammonia and production of comenic acid.

It forms readily-crystallizable salts with a certain proportion of ammonia, potash and soda; these have an acid reaction. The acid remains completely in solution in a small quantity of water when supersaturated with any alkali; if ammonia be employed and the fluid be evaporated to dryness at 212°, the salt with acid reaction remains.

It dissolves the earthy carbonates with effervescence when heated with them in water; if the acid be in excess, a crystalline salt with an acid reaction is obtained; if the carbonate predominate in quantity, almost the whole acid remains undissolved as some basic compound.

A solution of the crystalline ammonia salt gives with nitrate of silver a white gelatinous precipitate, which partially decomposes in boiling water. The same solution made alkaline gives with nitrate of silver a yellow flocky precipitate, which almost instantly passes through deepening shades of colour into a heavy black amorphous precipitate. The same solutions give with acetate of lead heavy insoluble precipitates; the acid solution gives with sulphate of copper a gray precipitate.

* I have also obtained this substance from meconate of ammonia; the details of my experiments will be given in a future paper on the subject of some derivatives of meconic acid.

I have examined more fully and analysed two or three of the salts of comenamic acid.

Comenamate of Ammonia.—Comenamic acid dissolves readily in ammonia when the alkali is added in excess, and such a fluid deposits no salt on standing; but if ammonia be added to a boiling aqueous solution of the acid in such quantity that the reaction remains slightly acid, the ammonia salt crystallizes out on cooling of the fluid in small grains, which when magnified are found to consist of bundles of needles radiating from a centre. They are difficult of solution in boiling water, but do not always reappear quickly when the liquid is cold. Their solution shows the phænomenon of epipolic dispersion very beautifully when rendered alkaline by ammonia. They are anhydrous:—

Carbon	41·56	12 =	72	41·86
Hydrogen	4·83	8	8	4·64
Oxygen	..	8	64	37·23
Nitrogen.....	16·14	2	28	16·27

The above analysis leads to the formula $NH^4O, NH^2C^{12}H^2O^7$.

Comenamate of Baryta.—The salt I analysed was obtained by adding a solution of the ammonia salt to chloride of barium; a precipitate was obtained in radiated groups, which on crystallization from boiling water assumed the form of separate prisms. It had an acid reaction, and furnished on analysis—

Carbon	30·20	12 =	72	29·92
Hydrogen	2·68	6	6	2·82
Oxygen	..	9	72	30·62
Nitrogen	..	1	14	5·81
Baryta	32·02	1	76·64	31·83

The formula deduced from the analysis of this substance, supposing it to be the neutral salt of a monobasic acid, will be $BaO, NH^2C^{12}H^2O^7 + 2HO$.

Comenamate of baryta, precipitated from an alkaline solution of the ammonia salt by chloride of barium, falls as a heavy white powder, insoluble in boiling water. Its analysis is subjoined:—

Carbon	22·93	12 =	72	23·35
Hydrogen	1·80	5	5	1·62
Oxygen	..	8	64	20·77
Nitrogen.....	..	1	14	4·54
Baryta.....	50·29	2	153·28	49·72

From this analysis it follows that to assimilate this salt to the last, it must be considered as a basic compound in which one of the equivalents of water retained at 212° is replaced by an atom of baryta, according to the formula $BaO, NH^2C^{12}H^2O^7 + BaO\,HO$. As precipitated from water, it contains an additional equivalent of water, having lost at 212°, 3·08 per cent.; the formula $BaO, NH^2C^{12}H^2O^7, BaO\,HO + Aq$ requires 2·83.

The salts of lime are very similar in appearance to the above, and with every base this acid seems to form two salts, which is a curious fact, since, reasoning from analogy, a substance originating as it does should be monobasic in its nature. I am not at present able to afford any further information on the subject of its constitution

and products of decomposition; but I may mention that I have observed in its behaviour under certain circumstances phænomena which I believe may prove of sufficient interest to encourage investigation.

These experiments were performed in the laboratory of Dr. T. Anderson of Edinburgh.

Cement for Stone-Ware. By M. Heller.

Gelatine is allowed to swell in cold water, the jelly warmed, and so much recently-slacked lime added as requisite to render the mass sufficiently thick for the purpose. A thin coating of this cement is spread while warm over the gently-heated surfaces of fracture of the articles, and let dry under a strong pressure. What oozes out is removed directly with a moist rag.—*Central-Blatt.*, No. 31.

Upon the Quantity of Phosphoric Acid existing in Healthy Urine. By Dr. D. Breed.

Notwithstanding the importance attached to every increase of our knowledge relating to physiology and pathology, hitherto an extended examination of the quantity of phosphoric acid in the urine has not been carried out by either a chemist or physician. A method, given by Prof. Liebig, for determining phosphoric acid accurately and quickly, enabled me to supply this deficiency, and to elicit some facts which may be of importance in the treatment of diseases.

This method consists in treating the urine with a solution of known strength of perchloride of iron until a small quantity of the mixture, when filtered and tested with ferrocyanide of potassium, gives a blue colour. It is based upon the fact, that a liquid containing phosphoric acid, both when neutral and when acidified with acetic acid, yields an insoluble precipitate with a solution containing peroxide of iron. The solution of perchloride of iron is best prepared by dissolving 15·536 grms. of iron in muriatic acid with the addition of nitric acid, evaporating to dryness in the water-bath to remove the excess of acid, and then dissolving the remaining acid in 2000 cub. centims. of water. 1 cub. centim. of this solution precipitates 10 milligrms. of phosphoric acid. Instead of this solution of perchloride of iron, one of indefinite concentration may also be used, the strength of which may be ascertained by testing with a solution of phosphate of soda, the quantity of phosphoric acid contained in which is known. The solution of perchloride of iron used must be perfectly free from the protochloride.

If the urine, the amount of phosphoric acid in which we are about to determine, has acquired an alkaline reaction from the decomposition of the urea, a portion of the phosphoric acid may have been precipitated in combination with lime or magnesia, and the precipitate must then be dissolved by the addition of a few drops of muriatic acid. The urine is measured and well shaken; a measured quantity, about 100 cub. centims. (or more), is drawn off with a pipette, and placed in a beaker, and acetate of soda (in considerable quantity if muriatic acid has been added) and acetic acid are added. The solution of the perchloride of iron is then added by means of a

burette, and the mixture is frequently tested to ascertain if all the phosphoric acid is precipitated, until a trace of the iron solution has been added in excess. To detect the latter, a piece of filtering paper imbued with ferrocyanide of potassium is placed upon a white porcelain surface (or upon a glass plate with a piece of white paper lying beneath it), and a doubled piece of filtering paper pressed against it with a glass rod from which a drop of the urine is hanging; if the urine contains an excess of the solution of iron, a blue colour is produced within from three to four seconds. The quantity of the solution of iron used is noticed. Two other portions are treated in exactly the same way; if the results agree, the quantity of the solution of chloride of iron which would have been required for the entire quantity of urine is calculated, and the amount of phosphoric acid corresponding to this quantity of the solution of iron is contained in the urine, and is then ascertained. By this method a physician who has but little spare time can easily make several determinations of the phosphoric acid in urine every day.

The quantity of phosphoric acid in the urine of a man in health and living a regular life, is nearly constant; but recent experiments have shown that the mode of living, as also diseases and medicines cause a variation in the amount of phosphoric acid in the urine.

The following results were obtained by the author:—

A. *Urine of Twenty-four hours.*

1. *Urine of four different Persons (but mostly one and the same).*

Urine of 24 hours.	Phosphoric acid.	Urine of 24 hours.	Phosphoric acid.
1645 cub. cent.	2·118 grms.	1607 cub. cent.	3·931 grms.
1150 ...	2·909 ...	2075 ...	4·336 ...
1690 ...	3·454 ...	1208 ...	2·719 ...
1675 ...	2·611 ...	1640 ...	2·837 ...
1462 *	3·647 ...	2655 ...	6·051 ...
1462 *	3·647 ...	1777 ...	3·126 ...
1707	3·744 ..	2058 ...	3·888 ...
1707 ...	3·744 ...	1768 ...	3·407 ...
1701	6·447 ...	985 ...	3·384 ...
1701 ...	6·447 ...	1561 ...	3·941 ...
1380	2·862 ...	1916 ...	4·946 ...
1380 ...	2·862 ...	740 ...	2·523 ...

On the average, 1000 cub. centims. of urine contain 2·317 grms. of phosphoric acid, or in twenty-four hours we have 1610 cub. centims. of urine and 3·732 grms. phosphoric acid.

2. *Urine of a Man who drank a large quantity of Water.*

Urine of 24 hours.	Phosphoric acid.
2478 cub. centims.	4·288 grms.
2407 ...	4·274 ...
1548 ...	4·006 ...
1919 ...	4·344 ...

* The quantity of urine passed during two intervals of twenty-four hours was ascertained, and half of this regarded as expressing the quantity passed during twenty-four hours.

1000 cub. centims. of urine correspond to 2·027 grms. of phosphoric acid, or for twenty-four hours we have 2086 cub. centims. of urine and 4·228 grms. of phosphoric acid.

3. *Urine of a Man who drank but little Water.*

Urine of 24 hours.	Phosphoric acid.
787 cub. centims.	3·807 grms.
1220 ...	4·218 ...
950 ...	3·904 ...
997 ...	4·133 ...

1000 cub. centims. of the urine contain 4·062 grms. phosphoric acid, or for the twenty-four hours we have 988 cub. centims. of urine and 4·015 grms. of phosphoric acid.

B. *Urine passed during the Day and after Sleep.*

1. *Urine of different Persons.*

Urine after sleep.		Phosphoric acid.	Urine during the day.		Phosphoric acid.
627 }	cub. cent.	1·472 grm.	835 }	cub. cent.	2·174 grms.
627 }		1·472 ...	835 }		2·174 ...
650 }		1·169 ...	1057 }		2·575 ...
650 }	...	1·169 ...	1058 }	...	2·576 ...
671 }		2·385 ...	1030 }		4·061 ...
671 }	...	2·385 ...	1030 }	...	4·062 ...
635 }		0·999 ...	745 }		1·904 ...
635 }	...	0·999 ...	745 }	...	1·904 ...
980	...	1·611 ...	1078	...	2·277 ...
540	...	1·033 ...	1236	...	2·374 ...
360	...	1·258 ...	625	...	2·127 ...
—	...	— ...	765	...	2·367 ...
450	...	1·223 ...	1103	...	2·718 ...
325 }		0·634 ...	—	...	—
325 }	...	0·634 ...	—	...	—
462	...	0·927 ...	1454	...	4·019 ...
185	...	0·528 ...	555	...	1·796 ...
415	...	1·364 ...	—	...	—

2·284 grms. of phosphoric acid correspond to 1000 cub. centims. of phosphoric acid.

2·763 grms. of phosphoric acid correspond to 1000 cub. centims. of urine.

2. *Urine of a Man who drank a large quantity of Water.*

Urine after sleep.	Phosphoric acid.	Urine during the day.	Phosphoric acid.
1050 cub. cent.	1·351 grm.	1420 cub. cent.	2·936 grms.
910 ...	1·496 ...	1497 ...	2·781 ...
230 ...	0·827 ...	1318 ...	3·179 ...
435 ...	0·934 ...	1484 ...	3·410 ...

1·755 grms. of phosphoric acid correspond to 1000 cub. centims. of urine.

2·130 grms. of phosphoric acid correspond to 1000 cub. centims. of urine.

3. *Urine of a Man who drank but little Water.*

Urine after sleep.	Phosphoric acid.	Urine during the day.	Phosphoric acid.
245 cub. cent.	1·132 grm.	542 cub. cent.	2·674 grms.
377 ...	1·549 ...	843 ...	2·668 ...
435 ...	0·983 ...	— ...	—
382 ...	1·516 ...	615 ..	2·617 ...

3·599 grms. of phosphoric acid correspond to 1000 cub. centims. of urine.

3·979 grms. of phosphoric acid correspond to 1000 cub. centims. of urine.

C. *Urine passed before and after Dinner (excluding the hours of Sleep).*

1. *Urine of different Persons.*

Urine before dinner.	Phosphoric acid.	Urine after dinner.	Phosphoric acid.
360 } cub. cent.	0·995 grm.	260 } cub. cent.	0·908 grm.
360 }	0·995 ...	260 }	0·908 ...
815 ...	1·377 ...	263 ...	0·901 ...
919 ...	1·510 ...	317 ...	0·863 ...
405 ...	1·415 ...	220 ...	0·712 ...
585 ...	1·595 ...	180 ...	0·772 ...
803 ...	1·485 ...	300 ...	1·233 ...
612 }	1·510 ...	492 ...	2·174 ...
613 } ...	1·510 ...	310 ...	1·274 ...
962 ...	1·845 ...	—	—
245 ...	0·722 .	—	—

2·239 grms. of phosphoric acid correspond to 1000 cub. centims. of urine.

3·745 grms. of phosphoric acid correspond to 1000 cub. centims. of urine.

2. *Urine of a Man who drank a large quantity of Water.*

Urine before dinner.	Phosphoric acid.	Urine after dinner.	Phosphoric acid.
960 cub. cent.	1·447 grm.	460 cub. cent.	1·490 grm.
1212 ...	1·826 ...	280 ...	0·955 ...
363 ...	1·164 ...	955 ...	2·011 ...
1004 ...	1·733 ...	480 ...	1·678 ...

1·743 grm. of phosphoric acid correspond to 1000 cub. centims. of urine.

2·820 grms. of phosphoric acid correspond to 1000 cub. centims. of urine.

3. *Urine of a Man who drank but little Water.*

Urine before dinner.	Phosphoric acid.	Urine after dinner.	Phosphoric acid.
360 cub. cent.	1·627 grm.	182 cub. cent.	1·047 grm.
620 ...	1·751 ...	223 ...	0·916 ...
560 ...	1·473 ...	—	—
230 ...	0·891 ...	385 ...	1·725 ...

3·244 grms. of phosphoric acid correspond to 1000 cub. centims. of urine.

4·541 grms. of phosphoric acid correspond to 1000 cub. centims of urine.

Dr. Breed found phosphoric acid in a liquid which Prof. Vogel obtained by the operation of *paracentesis abdominis*. 3105 cub. centims. of the liquid gave 4·648 grms. of phosphoric acid. The urine of twenty-four hours from this patient contained only 1·2 grm. of phosphoric acid.—*Ann. der Chem. und Pharm.*, vol. lxxviii. p. 150.

PROCEEDINGS OF SOCIETIES.

British Association for the Advancement of Science.—Meeting held at Ipswich, July 2nd, 1851.

On the Products of the Action of Heat on Animal Substances. *By* Dr. T. Anderson.

Dr. Anderson having discovered picoline in coal-tar, was led to investigate the well-known and peculiar fœtid oil called bone-oil, and, to obtain the best results, operated in the last experiment upon 250 gallons of the distilled bone-oil, and discovered at least three different series of bases in the oil. In the first he had established the existence of the bodies called methylamine, æthylamine, butylamine, petinine, and probably others; in the second series, picoline, and other bodies of which it is the type. The third series is very remarkable, and all the members of it are characterized by decomposing by heat and excess of acid into bases of the picoline series, and a remarkable and peculiar red or orange-coloured resinous substance. This extensive investigation was not yet concluded; but the oil, besides these bases, contained benzole and the nitriles of some of the fatty acids.—*Athenæum.*

On the Action of Superheated Steam upon Organic Bodies. *By* Prof. Scharling *of Copenhagen.*

This communication was read by Dr. T. Anderson, who exhibited a drawing of apparatus employed*.

In the discussion on these communications, relating as they do not only to the purification of substances, but suggesting new modes of manufacturing (such as the production of carbon for gunpowder by high-pressure steam), Mr. Mallet alluded to the astonishing effects of high-pressure steam in the peat process. It appears that in Prussia steam at 60 lbs. pressure is used, and passed through hot pipes to obtain at least 600° of heat, and is then thrown into compressed peat, where it produces the effect of a "fiery sponge," robbing the peat of water, carbonizing the material, and effecting the complete distillation of many substances. The texture of the peat is so far changed and peculiar, that it is rendered pyrophoric, and takes fire by exposure to air, and it is necessary to cool down the charcoal in an atmosphere of steam.—*Athenæum.*

* This communication will be given in one of our next Numbers, the MS. having been kindly placed in our hands by the Author.—Ed.

THE CHEMICAL GAZETTE.

No. CCXV.—October 1, 1851.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

Researches on Human Fat, and on the Separation of the Fatty Acids from each other. *By* Dr. Heintz.

In an experiment to prepare margaric acid from human fat, which is said by Chevreul to consist solely of margarine and oleine, the author found that the fatty acids obtained from it, however frequently crystallized from the alcoholic solution, never furnished an acid which had its melting-point at 140° F. It never could be raised higher than 133°. This acid however is not pure, but a mixture of several. The usual method followed in order to obtain these acids, or only one of them, in a pure state, that of recrystallizing from the alcoholic solution, is not satisfactory. The author therefore sought to discover some other method by means of which this separation might be effected. The properties however of these acids, as also of their compounds, are so much alike, that the endeavour to base a method of separation upon the principles hitherto in use proved vain.

Turning to account the method recently proposed by Liebig* for the separation of the volatile acids, the author succeeded in ascertaining the nature of the mixture. This method, which is simply the following, is undoubtedly susceptible of further extension. When a mixture of substances is treated with a substance for which they all have affinity, but not in sufficient quantity to saturate the whole, those whose affinity is greatest will combine therewith. It is evident that this principle can be applied in the separation of those substances which have very similar properties, not only in the free state, but likewise in their compounds. However much these may resemble each other, there will almost in every case be produced some compound possessing such different properties from the uncombined substance that the portion of the substance which has entered into combination may be separated from that which has remained in the free state.

According to Heintz, the fatty acids are dissolved in so much boiling alcohol that no separation takes place on cooling; to the boiling solution crystallized acetate of lead, which has been previously dissolved in alcohol, is added in small quantities at a time,

* Chem. Gaz., vol. viii. p. 24.

in the proportion of a third part by weight of the acid mixture. Should a precipitate form in the boiling solution, some acetic acid is added until the solution has again become clear; it is then allowed to cool, the precipitate which forms brought upon a filter, and pressed. The liquid filtered from the precipitate is mixed with a small excess of an alcoholic solution of acetate of lead, filtered, and the precipitate likewise submitted to pressure.

The lead salts obtained in this manner are decomposed either by boiling with a very dilute hydrochloric acid, or, as this decomposition proceeds very slowly, on account of the sparing solubility of the chloride of lead, by hot alcohol to which some hydrochloric acid is added. However, on account of the possible formation of æthers of the fatty acids, the alcoholic solution must be boiled with caustic potash, and after the alcohol has been expelled by evaporation the potash-soap decomposed by hydrochloric acid.

Each of the portions thus obtained is again separated in the same manner into two, and each of these four again into two; and when both the portions last separated have still a very different melting-point, they must be further submitted to the same treatment. The different portions of acid must finally be purified by recrystallization from alcohol, and this operation repeated until the melting-point no longer varies.

The above-described method of separation moreover admits of our ascertaining whether the acids are really pure or not; for instance, on being separated into two portions, they must, if they are chemically pure, exhibit no difference in the melting-point.

The author has succeeded by this method in proving that the supposed pure stearine, which is obtained when mutton-fat is recrystallized from a solution in æther until the melting-point no longer varies, is not a pure substance. The acid prepared from it. by saponification melts, for instance, at 147°, and can be separated by the above treatment into two portions of acid, one of which melts at 133° and the other at 153°.

The same is the case with the supposed pure cetine, which is procured in a similar manner from spermaceti, and which is said to melt at 120°–121°. The circumstance that the author succeeded in preparing a cetine by very frequently repeated recrystallization, the melting-point of which was situated at 128°, shows that the above substance was not pure. The fatty acid prepared by the saponification of cetine, which melted at 120°, with an alcoholic solution of potash, and from which the simultaneously-formed æthal has been removed, can be decomposed by acetate of lead into two portions of acid, one of which melted at 129° and the other at 114°.

The results which the author has obtained in the examination of human fat most completely prove the applicability of this new method of separation. By means of it he succeeded in separating no less than four distinct acids from the solid fatty acid of human fat, which he had procured by submitting the crude acid mixture alone, and again after it had been dissolved in a little hot alcohol and then exposed to the cold, to repeated pressure.

The first, which is most easily precipitated in combination with oxide of lead, is only present in very small quantity; only about 0·2 grm. was obtained in an apparently pure state from more than 2 lbs. of human fat. It was impossible to be convinced of its perfect purity from so little being obtained; however, it separated from the alcoholic solution in small laminæ, generally in spherical groups, and when it solidified after being melted it assumed a crystalline scaly appearance. It melted at 156°, and furnished on analysis numbers which agree very well with the formula $C^{36}H^{36}O^4$. The author hopes to meet with this acid in greater abundance in mutton and beef fat, and then to determine its nature more accurately.

A second acid, which is next readily precipitated in combination with oxide of lead, is apparently a new acid; the author calls it *anthropic acid*, and the corresponding glycerine compound *anthropine*. Of this acid only about 1 grm. was obtained from the above-mentioned quantity of fat in the pure state. But yet, in comparison with the other solid fat acids, it is not present in small quantity in the human fat. It crystallizes in beautiful broad laminæ, which often possess a mother-of-pearl lustre. It melts at 133°; on cooling, it solidifies into beautiful laminar crystals. It has not been possible to place its composition beyond doubt as yet from want of material, and because the relations which the analysis of the acid itself and of the baryta and silver salts appears to have demonstrated are of a somewhat unusual kind. To bring the results of the analyses into accordance, the acid itself must consist of $C^{34}H^{31}O^3 + HO$, the silver salt of $C^{34}H^{31}O^3 + AgO$, and the baryta salt of $C^{34}H^{31}O^3 + BaO + HO$.

The third acid which Heintz procured from human fat is margaric acid, which was obtained with all its well-known properties, and the composition $C^{34}H^{34}O^4$.

Lastly, the fourth acid, and which according to all appearance exists in the greatest proportion in human fat, is palmitic acid, and which consequently is not restricted to the vegetable kingdom. Of the four acids, it has the least affinity for oxide of lead. It crystallizes from the alcoholic solution in small scaly crystals, melts exactly at 143°·6, and solidifies on cooling, not into needles, but in the form of aggregrated crystalline scales. A small admixture of margaric acid however imparts to it the property of solidifying on cooling into acicular crystals; but between the needles the whitish, scaly, palmitic acid is distinctly perceptible. The analyses lead to the formula $C^{32}H^{32}O^4$.

The author has also submitted the fluid portion of human fat to examination. The oleate of baryta, prepared according to the method described by Gottlieb, constantly contained more baryta than corresponds to the formula proposed by him; instead of 21·9 per cent., Heintz found 22·2 and 22·5; and on exhausting with so little boiling alcohol that never more than a part of the salt was dissolved, portions of baryta salt separated, which furnished at last 22·7 per cent. baryta. By exhausting with æther, a minute quan-

tity of a salt containing much more baryta was removed, and the insoluble portion was now pure oleate of baryta.

The author has made another most interesting observation. When, for instance, human fat is separated in winter from the solid parts, and the liquid portion is let stand till the next winter, solid fat is again deposited, a phænomenon which may be repeatedly observed with the same fat. It would be thought that in this case margarine had been formed from oleine, but this is not so. If, for instance, this solid fat is separated as much as possible by pressure and other suitable operations, from the liquid portion, the residue dissolves very readily in a hot solution of carbonate of soda in much water; it does not consist therefore of fat, but of fatty acid, and the author has detected in it anthropic, margaric and palmitic acids.—*Proc. Berlin Acad.*, 1851, p. 484.

On a new Acid derived from Valerianic Acid. By P. Dessaignes.

As well known, valerianic acid is very little altered by the action of nitric acid. I wished to ascertain what would be produced by the long-continued reaction of these two acids. In the same apparatus as that which I employed to convert butyric into succinic acid, and for eighteen days without interruption, I heated nearly to ebullition a mixture of monohydrated nitric acid and valerianic acid, both that extracted from valerian and that obtained with amylic alcohol by Balard's process. I added from time to time some nitric acid, so as to keep the volume of the mixture nearly constant. The products of this reaction varied in different operations. The most abundant substance, excepting the valerianic acid itself, which remains for the greater part unaltered, is the acid which forms the subject of the present notice, and which is equally obtained from the valerianic acid from the two different sources. With the acid from valerian there is simultaneously produced another deliquescent acid, and a neutral crystalline substance containing nitrogen and possessing a slight odour of camphor. With the acid from the oil of potatoes a neutral nitrogenous oil of a camphorated odour is likewise obtained. The result of my researches on these different products I shall communicate on some future occasion.

The mixture contained in the retort was submitted to distillation. The first half of the condensed liquid contains a colourless acid oil, which decreases considerably by washing, and which becomes neutral and solid or liquid according to the origin of the acid employed. On continuing the distillation, the retort is filled anew with copious red fumes; the operation is then discontinued, and the residue gently heated in a dish until it has attained the consistence of syrup. After some time thin crystals form in it, which are freed from mother-liquor by pressure between blotting-paper, and which are easily purified by being recrystallized once or twice.

This acid, when perfectly pure, crystallizes in superb rhombohedral prisms, which frequently overlie each other like the tiles of a roof. It begins to sublime at 212° F., but its boiling-point is far

higher. It dissolves very readily in hot, much less in cold water, on the surface of which the crystals sometimes perform gyratory motions.

The lead salt is very soluble, and crystallizes in thin prisms. The baryta salt is soluble. The lime salt crystallizes in needles, which dissolve easily, rotating upon the water. The persalt of iron resembles the succinate. The silver salt is a light precipitate, which dissolves in boiling water, and crystallizes on cooling in thin brilliant prisms.

The acid dried *in vacuo* and its silver salt dried at 212° were analysed with oxide of copper and the addition of metallic copper. The nitrogen could not be determined in the form of ammonia. From want of a pump I had recourse to the process of M. Dumas, of expelling the air in the tube by a current of carbonic acid. The following results were obtained:—

For the acid.		For the silver salt.	
Carbon.....	40·93	Carbon.....	23·61
Hydrogen	6·18	Hydrogen	3·63
Nitrogen	10·12	Silver	42·27

The preceding numbers agree pretty well with the numbers representing the composition of nitrovaleric acid, and which for the formula $C^{10} H^{18} N^2 O^8$ are—

Carbon.....	40·81	Carbon.....	23·62
Hydrogen	6·12	Hydrogen	3·15
Nitrogen	9·52	Silver	42·52

It is however possible, and the physical properties of this new acid would lead me to believe, that it is nitroangelic acid, the formula of which would be $C^{10} H^{14} N^2 O^8$, which would require 41·37 per cent. C, 4·82 H, and 9·65 N.—*Comptes Rendus*, August 11, 1851.

On the Action of the Nitrite of Potash on the Nitrate of Cobalt. By E. Saint-Evre.

When nitrite of potash dissolved in water is poured gradually into a solution of nitrate of cobalt rendered acid by nitric acid, a considerable quantity of deutoxide of nitrogen is disengaged, and forms with the oxygen of the atmosphere red fumes. Crystals of nitrate of potash soon form in the liquid if it is sufficiently concentrated; at the same time it becomes colourless, and deposits a crystalline powder of a beautiful yellow colour, which furnished on analysis numbers leading to the formula represented in equivalents by $N^2 O^{10} CoK$.

The following are the reactions of this new salt of cobalt:—When suspended in water, it is not decomposed in the cold by sulphuretted hydrogen. Chlorine does not attack it in the cold; it requires the temperature to be raised to 212° for the rose colour peculiar to the salts of cobalt to be manifested. It is anhydrous, almost insoluble in water at the ordinary temperature, as well as in nitric and hydro-

chloric acids, which decompose it only on ebullition, with disengagement of red vapours. Boiled for a long time with water, it finally dissolves, acquiring a rosy tint, with disengagement of acid colourless vapours. The evaporated liquid furnishes a new salt of a lemon colour, distinct from the preceding. Treated with hydrogen in a glass bulb over an alcohol-lamp, it first gives off vapours, and then a large quantity of ammonia. On treating the residue with water, metallic cobalt and an alkaline liquid holding cobalt in solution are obtained. Calcined in a current of nitrogen, it liberates deutoxide of nitrogen, and leaves a residue of black oxide, which on being placed in contact with hydrochloric and oxalic acids liberates chlorine with the one and carbonic acid with the other. Boiled with an aqueous solution of potash, it deposits an oxide possessing the same properties.

Some experiments, made several months ago, tend to show that this new salt of cobalt will furnish the painter with a most useful colour, possessing in a high degree the qualities sought for by artists.

I have hitherto only been able to determine the relations by weight of the elements constituting this new and singular compound, and must reserve the question as to the degree of oxidation of the nitrogen and cobalt for some future occasion. The use of deoxidizing agents, such as sulphurous acid, and a more minute examination of the reactions of this double salt, lead me to hope that this question will soon be solved.—*Comptes Rendus*, August 11, 1851.

On the Composition of Ricinolamide, and the Production of Caprylic Alcohol. By J. Bouis.

Castor oil, which was submitted to examination by Bussy and Lecanu, has since been investigated by a great number of chemists, but the subject is far from being exhausted. Some researches on this substance, commenced in 1845 in the laboratory of M. Dumas, and since continued in that of M. Peligot, have furnished me with results which the investigations of Bussy, Tilly, Williamson, Svanberg and Kolmodin, Saalmüller and Playfair render it unnecessary for me to mention. I intend discussing them in a lengthy memoir, together with my own observations.

On describing the formation of margaramide, M. Boullay stated that several oils experienced an analogous metamorphosis by the action of ammonia; but he went no further. I will now proceed to describe the various products to which the action of ammonia on castor oil gives rise.

Castor oil, placed in contact with a solution of ammonia in alcohol, or merely in water, forms a solid compound, which represents the amide of ricinolic acid. This ricinol-amide is solid, white, crystallizes in mammillated groups, melts at 151° F., is insoluble in water, but soluble in alcohol and æther. It burns with a very smoky flame, is not acted upon in the cold by potash, but when heated it liberates ammonia if the potash is very concentrated, and forms

ricinolate of potash. This amide is decomposed in the cold by acids being resolved into ricinolic acid and an ammonia salt of the acid employed. Its composition is expressed by the formula $C^{36}H^{35}NO^4$, which represents the ricinolate of ammonia minus the elements of water.

Ricinolic acid, obtained by saponification, is represented by $C^{36}H^{34}O^6$; the analyses of the salts of silver and baryta confirm this composition. The presence of this acid was pointed out by Messrs. Svanberg and Kolmodin in castor oil.

When the amide is saponified by potash, the reaction commences only at the moment when the potash losing its water begins to fuse; a volatile liquid is then disengaged simultaneously with the production of hydrogen. On treating the mass with water and precipitating by hydrochloric acid, a mixture of acids separates on the surface, one of which is liquid and the other solid, which is the sebacic acid discovered by M. Thénard.

The sebacic acid thus obtained forms white crystalline spangles, and melts at 261°. The analysis of this acid agrees perfectly with the formula $C^{20}H^{18}O^8$, assigned to it by MM. Dumas and Peligot.

From the ricinolic and sebacic acids being always associated in this reaction, it was important to ascertain whether the two acids formed part of the amide, or whether the sebacic acid was produced at the expense of the other. I have found that sebacic acid is a product of decomposition of ricinolic acid. In fact, by distilling ricinolic acid or ricinolate of potash with highly concentrated solution of potash, there is formed sebate of potash, hydrogen, and the volatile oil described below.

Hitherto sebacic acid has been prepared by the distillation of oleic acid, or of certain fatty bodies containing oleine. This operation, which is a most unpleasant one on account of the odour, yields moreover the sebacic acid in very small quantity. Its preparation from ricinolamide would require too much time, as this takes from two to three months to be well formed. I then tried to obtain it directly by treating the castor oil with very strong potash, and the experiment proved perfectly successful.

In this process the disagreeable odour resulting from the decomposition of fatty bodies is replaced by the pleasant and aromatic odour of the volatile oil which is formed. In an industrial point of view sebacic acid may meet with some useful applications if it can be produced at a low price, of which I have no doubt. Its high melting-point and ready combustion will certainly allow of its being associated with more fusible substances for the manufacture of candles.

The proportion of volatile oil appears to be constant. Several experiments repeated upon various quantities of castor oil of different origin constantly furnished a fifth in weight of volatile oil.

This volatile oil forms a transparent oily liquid, which stains paper like the essential oils, is insoluble in water, soluble in alcohol, æther and acetic acid. It has an agreeable aromatic odour, and burns with a very beautiful white light. Its specific gravity is 0·823 at

66°; at 356° it boils without decomposition. Its composition agrees with the formula $C^{16}\,H^{18}\,O^2$. The theoretical density of the vapour is 4·49; experiment yielded 4·50=4 vols.

Sulphuric acid dissolves the oil, and yields crystalline salts of lime and baryta soluble in water. On the application of heat, sulphuric acid converts it into carburet of hydrogen, isomeric with olefiant gas and amylene. The carburetted hydrogen is very mobile, lighter than water, burns with a very beautiful flame, and boils at 257° without decomposition. Its composition is represented by $C^{16}\,H^{16}$. The theoretical density of its vapour is 3·26; experiment gave 3·90=4 vols.

Fused chloride of zinc gives rise to the production of several isomeric hydrocarbons, varying among themselves by their state of condensation; but the one most abundant and the most volatile boils at 257°, and possesses the same properties as that obtained with sulphuric acid. The density of its vapour was found to be 3·82 =4 vols.

Chloride of calcium dissolves in the volatile oil, and furnishes very beautiful transparent crystals, which are decomposed by the action of heat or by the addition of water into chloride of calcium and volatile oil. The compound is less soluble in the cold than when warmed.

The action of nitric acid varies according to its strength; with dilute acid I converted the whole of the volatile oil into a volatile liquid acid, but the continued action of the acid produced pimelic, lipic, succinic and butyric acids.

Acetic and hydrochloric acids convert the oil into æthers, possessing a highly aromatic fruity odour. The æthers are decomposed by potash into the volatile oil and a salt of the corresponding acid employed.

Caustic lime at a high temperature decomposes the oil into hydrogen and gaseous hydrocarbons. Potash-lime and soda-lime have no action upon the oil at 482°; but above that temperature very pure hydrogen is disengaged, and a volatile acid is formed, which remains in combination with the potash.

These facts evidently prove that the oil belongs to the class of alcohols; it is the caprylic alcohol, $C^{16}\,H^{18}\,O^2$, and takes its place in the following series between the amylic and the æthalic alcohols:—

$C^2\,H^4\,O^2$, methylic alcohol.
$C^4\,H^6\,O^2$, vinic alcohol.
$C^{10}\,H^{12}\,O^2$, amylic alcohol.
$C^{16}\,H^{18}\,O^2$, caprylic alcohol.
$C^{32}\,H^{34}\,O^2$, æthalic alcohol.

The way in which caprylic alcohol is formed will be seen by the following equation:—

$$\underset{\text{Ricinolic acid.}}{C^{36}\,H^{34}\,O^6} + 2(KO,HO) = \underset{\text{Sebate of potash.}}{C^{20}\,H^{16}\,K^2\,O^8} + \underset{\text{Caprylic alcohol.}}{C^{16}\,H^{18}\,O^2} + 2H.$$

Comptes Rendus, August 11, 1851.

✓ *Chemical Examination of* Aspidium filix mas, *and* Asplenium filix fœmina. *By* H. Bock.

The author has submitted to examination the fronds and roots of these two well-known ferns.

The *root* of *Aspidium filix mas* furnished, on distillation of 10 lbs. of fresh root, 8 grs. of an essential oil, which was of a reddish colour, similar to oil of cinnamon, with an aromatic and pungent after-taste and a peculiar odour. It is readily soluble in æther and absolute alcohol; lighter than water, to which it imparts the odour of the powder of the fresh root. Concentrated sulphuric acid coloured it reddish-brown; strong muriatic acid bleached it; iodine coloured it blackish-brown, but did not explode with it.

To estimate the *proteine compounds*, the *starch* and the *gum*, 1600 grs. of the finely-cut fresh root were crushed to a uniform paste, with the addition of a very little water, pressed, and the operation repeated several times. The expressed liquids were let boil in a porcelain dish, and the liquid evaporated until something separated. The separated impure albumen was treated so long with boiling alcohol till nothing further was dissolved. It had a green colour. It was now treated with a mixture of alcohol and æther, then with pure æther, and lastly with small quantities of boiling water until what ran off no longer reacted with iodine. The residual mass was grayish-white, became darker on drying, and amounted on an average to 16·6 grs. On solution in caustic potash, it left 2·5 grs. of fibre, giving 14·1 grs. as the amount of pure albumen.

It was somewhat soluble in a large quantity of boiling water; perchloride of mercury produced in the solution a white precipitate; it dissolved in acetic acid on the application of heat. When the potash solution was boiled for some time, it acquired a brown colour; acetic acid then produced a gelatinous precipitate.

The residual root was left in the press-bag, placed in a marble mortar, and well pounded with renewed water until what passed off showed no reaction with iodine. The grayish-white turbid liquid was mixed with that which had been separated from the albumen. After some time it deposited a grayish-white precipitate, which was mixed with white bands of starch; the starch was scarcely at all granular, but almost mucilaginous. It was treated with æther, absolute alcohol and cold water; there remained 45·5 grs. On ebullition with dilute hydrochloric acid, it left 5·5 grs. of fibre, and furnished consequently 40 grs. of starch. When the liquid filtered from the starch was for the greater portion evaporated, and then mixed with alcohol, a flocculent precipitate was formed, which when dry had a conchoidal fracture, and consisted of gum, tannic acid and traces of salts. To obtain the entire amount of gum, the residual root was again repeatedly exhausted with boiling water, and the extract mixed with the first. The separation of the gum and the tannic acid from the salts was effected according to Schmidt's method, by repeated solution in water, and precipitation with alcohol containing hydrochloric acid. In order not to render the tannic

acid insoluble, the alcohol at first was mixed with only a little hydrochloric acid, and more acid added after removal of the tannates. The gum, thus purified and washed with alcohol, weighed 138 grs. It was of a yellowish-brown colour, readily soluble in water, was not rendered thick by a solution of borax, furnished precipitates with the basic and neutral acetates of lead, was rendered somewhat turbid by a solution of silicate of potash, and gave a white precipitate with protonitrate of mercury.

The *tannic acid* was contained in the extract obtained by exhausting the root first with water, and then with water containing hydrochloric acid. It was precipitated with gelatine, the precipitate dissolved in dilute caustic potash, and then thrown down with peracetate of iron. In another case, the hydrochloric extract was immediately neutralized with potash, and precipitated with acetate of iron. From the loss on ignition of the iron precipitate, the author calculates 19·9 grs. of tannic acid for 800 grs. of fresh root. The tannic acid however contained some gallic acid.

Ætherial Extract of the Root.—The root was exhausted in a small displacement apparatus with æther, and the æther then distilled off. It had acquired scarcely any odour, had a neutral reaction, and did not become turbid on being mixed with water. The extract from 2000 grs. of the powdered root was of a grayish-brown colour, very thick, and had separated into two layers, the upper one of which was oily and of a green colour, the lower one brownish and more resinous. On distillation with water, the product yielded a mere trace of essential oil to æther, and which resembled the oil above described. The residue was digested with water containing æther, the æther separated by distillation and the water by filtration. The filtered liquid was turbid, had an astringent taste, and left on evaporation 6·5 grs. residue, which dissolved readily in water excepting a few brown flakes. The concentrated solution had a feeble acid reaction. Solution of isinglass and albumen produced copious precipitates, perchloride of iron and peracetate of iron gave grayish-brown precipitates, and lime-water a reddish-brown precipitate, which did not dissolve in an excess. Nitrate of silver caused a bulky flocculent precipitate, and perchloride of mercury a light green precipitate. Consequently what the water had removed from the ætherial extract was a tannic acid, belonging to those which strike a green colour with iron.

The ætherial extract was now treated with alcohol of 0·840, first in the cold and then boiling. It acquired a reddish-brown colour, and left on evaporation 56·5 grs. of a reddish-brown resin, transparent at the sides, and which on long exposure to the air became darker, harder and brittle. On being heated, it soon softened and became liquid; it had a somewhat aromatic odour and bitter taste; it dissolved readily in æther and spirits, and was heavier than water. On mixing the spirituous solution with water, it became turbid, had an acid reaction, and some time elapsed before the resin separated. The resin dissolved readily in oil of turpentine and likewise in ammonia. Nothing separated from the solution on the application of heat. It

likewise dissolved in sulphuret of carbon; when heated with carbonate of potash, it dissolved in it, expelling the carbonic acid; it dissolved readily in caustic potash; the resin soap was very soluble in water, and was not separated by chloride of sodium even on ebullition. This resin consequently belongs to the strongly electronegative hard resins of Unverdorben. In order to separate completely the resin from the fat oil, the residual æther extract was treated with alcohol of 0·780, and what was left on evaporation digested with alcohol of 0·840. The complete separation of the resin from the oil is difficult, and can only be accomplished by solution in æther and alcohol of various strength. In this manner 10 grs. more of resin were separated. The fatty oil which now remained, after treating with water and spirits, was thick, dark green, and easily soluble in æther. The æther solution was poured into a narrow-necked flask, and the æther allowed to evaporate slowly in the cold. After some time, a verrucoid, yellowish-white mass had separated on the sides of the vessel. The oil was decanted, again dissolved in æther, and exposed to a temperature of 18°, and this operation repeated as long as anything separated. The adherent oil was removed from the solid mass by rinsing with a little cold æther. This substance, examined under a lens, appeared crystalline; but no definite crystalline form could be detected; it was inodorous and tasteless, adhered between the teeth like wax, was soluble in much æther, partially soluble in boiling alcohol of 0·780, but separated for the greater part on cooling. The solution was neutral. Oil of turpentine readily dissolved it; nitric acid has little action upon it; caustic potash dissolves it readily, and nothing separates on the addition of chloride of sodium. Concentrated sulphuric acid mixes with it, colours it reddish, and diffuses an odour of butyric acid. On pouring water into this mixture, a reddish precipitate fell. This substance has most resemblance to wax, and differs from it principally by its solubility in oil of turpentine. It appears to form a peculiar *stearine*, like those which separate from the fatty oils, after long standing and in the cold. It is most easily separated from the fatty oil after removal of the tannic acid and the resin; cold likewise facilitates the separation. After standing for one year, the above amount of oil had furnished 19·1 grs. of stearine; no further separation was observed.

The quantity of the fatty oil which now remained amounted to 108 grs. It had a dark green colour, but at first was bright green, probably owing to the presence of chlorophyll, which grew darker with time. It was of the consistence of oil of almonds, but did not congeal even at 9° F. The statement of Liebig, in Geiger's 'Handbuch der Pharmacie,' that the oil congealed like butter at 32°, is probably owing to the oil not having been pure, and still containing stearine and resin; its specific gravity at 59° is 0·942; it has a peculiar odour and a bitter taste. It is sparingly soluble in spirit of 0·820; alcohol of 0·780 dissolves some of it in the cold, and nearly the whole on the application of heat, but the greater portion of what has dissolved again separates on cooling. It has no acid reaction.

Treated with solution of caustic potash, it forms a greenish-brown soap, which floats upon the solution. By treating the dissolved soap with muriatic acid, oleine and margaric acid could be separated according to Chevreul's method. From the mother-liquor combined with the wash-waters, after the addition of sulphuric acid and separation of the sulphate of potash, glycerine was obtained. With the acid nitrate of the protoxide of mercury, the oil solidified. With fuming nitric acid of 1·55 it likewise formed a solid mass; it consequently belongs to the non-siccative oils.

The ætherial extract consists therefore of 7 parts tannic acid, 72·5 parts of resin, 108 of fatty oil and 19 of stearine.

Treatment of the Root with Alcohol.—It was exhausted in the same manner as stated with æther, first with alcohol of 0·780, then of 0·820, and lastly of 0·870. The first extracts were of a dark, the last of a pale yellowish colour. On evaporation, the residues differed only in colour, were inodorous, of a sweetish astringent taste, and had an acid reaction. Boiled with water, the whole dissolved except a gray albuminous mass, which after being well washed was yellowish-gray, very adhesive, inodorous and tasteless. It dissolved easily in boiling alcohol, and likewise in ammonia; from the latter solution acetic acid separated a grayish-white coagulum of vegetable gelatine or gliadine. After removal of the gliadine, the spirituous solution was evaporated to the consistence of honey, and set aside. After some time, numerous groups of crystals had formed, of the colour of brown sugar-candy; under the lens they appeared to be oblique four-sided prisms, truncated by two facets.

In order to separate the tannic acid from the sugar, sheets of isinglass were placed in the mixture, and the whole exposed to a moderately-warm temperature, so that the sheets swelled up and were partially dissolved. It was necessary to observe the point at which the whole of the tannic acid was precipitated and had combined to form tannate of gelatine; but in general somewhat more isinglass was dissolved than was requisite for the precipitation of the tannic acid. When this was the case, the sugary gelatine had to be evaporated nearly to dryness, and digested with hot alcohol of 0·780, the alcohol filtered, and this treatment repeated as long as any sugar was removed. The sugar was obtained from this solution by evaporating the alcohol. On being mixed with concentrated sulphuric acid, it turned blackish-brown, and was carbonized on being heated. Carbonate of soda added to a solution of the sugar scarcely altered the colour; but on the application of heat, it became somewhat darker. A dilute solution of caustic potash behaved in the same manner; nothing separated however from these mixtures; mixed with arsenite of potash, the solution of sugar was scarcely coloured at first; but after long standing, it became rose-red, and finally dark red. Nitrate of silver produced a turbidness, and after ebullition a brownish-black powder was deposited; heated with perchloride of gold, a yellowish precipitate, soluble in hydrochloric acid with a yellow colour, was formed. On the application of heat, the whole became black and thick. When a concentrated aqueous solution

was heated with verdigris, a large amount was dissolved with a dark green colour; caustic and carbonated potash produced no precipitate in this solution. By its capacity for crystallizing, and its behaviour towards acids and alkalies, it comes nearest to cane-sugar. The extract obtained from the root by alcohol consisted therefore of 198 grs. sugar, 7·2 vegetable gelatine, tannic acid, and a small amount of salts, which were determined in the analysis of the ashes.

Residue of the Root.—The residue, after driving off the alcohol, amounted to 554 grs. A portion of the albumen, the starch and the gum were extracted from it with cold and boiling water, according to the method above described. The residue was boiled with water containing some hydrochloric acid, and the filtered slightly-coloured liquid neutralized with ammonia. It acquired a lilac colour, and deposited a bulky precipitate. On calcining a portion of the well-washed precipitate, the ash dissolved with effervescence in nitric acid; the nitric solution, supersaturated with ammonia, deposited phosphate of lime; the liquid filtered from this gave, on the addition of oxalate of ammonia, a precipitate of oxalate of lime; the lime was contained in the root as tannate, and had been extracted by the hydrochloric acid. The liquid filtered from the precipitate by ammonia was evaporated down to a small volume and mixed with absolute alcohol, which produced a gelatinous mass, soluble in water and weak spirit, acquiring a yellowish-brown colour on desiccation, and resembled gum. It dissolved readily in caustic potash, and sulphate of copper produced no precipitate in the alkaline solution; the whole acquired a bluish colour, and deposited protoxide of copper. When the mass was boiled for some time in sulphuric acid, it became liquid, and furnished, after saturation of the acid with lime and removal of the gypsum, a sweetish residue, which proved to be dextrine, formed from the amylaceous fibre by ebullition with the acid; altogether 27 grs. were obtained. The liquid filtered from the dextrine furnished on evaporation no other organic substance.

The residue, after washing out the acid, was digested with dilute caustic potash; the filtered liquid was reddish-brown, but formed no deposit; it was saturated with dilute hydrochloric acid, when it acquired a much lighter colour, and congealed to a gelatinous mass. After some time it separated into two layers, the upper one of which was reddish-brown, and formed a thick jelly; the lower one was yellow and liquid; the mixture was brought upon a filter and washed; but as it was difficult to remove chloride of potassium from the jelly, it was repeatedly stirred with water and carefully pressed. After being well washed, it had an acid reaction, and resembled swelled bassorine. It was treated with concentrated acetic acid as long as anything was removed; there was left on evaporation 52 grs. of albumen coloured by tannin. The substance, freed from albumen, was pectic acid; it was well washed with water to remove the acetic acid, was again dissolved in caustic potash, and the pectate of potash mixed with pieces of carbonate of potash in order to

remove the brown colour, but without success. 38·6 grs. of pectic acid were obtained.

Ash Analysis.—The root was charred in a Hessian crucible, and then reduced to ash in a platinum crucible. 2000 grs. of the root furnished 42·6 grs. of ash.

All the constituents of the root arranged together give in—

1000 parts of dry root,	21 parts of ash,
0·4 essential oil.	1·1 sulphate of lime.
60·0 fat oil.	0·4 phosphate of magnesia ($MgO + PO^5$).
10·0 stearine.	1·6 phosphate of lime ($CaO + PO^5$).
40·0 resin.	2·2 chloride of calcium.
100·0 starch.	0·4 chloride of sodium.
4·0 vegetable gelatine.	0·1 silica.
35·0 albumen.	9·4 carbonate of lime.
33·0 gum.	5·5 carbonate of potash.
110·0 sugar.	0·3 loss and traces of perphosphate of iron.
100·0 tannic and gallic acids.	21·0
21·0 pectine.	
15·0 amylaceous fibre.	
21·0 ash.	
450·6 fibre and loss.	
1000·0	

The Frond of Aspidium filix mas.—The frond collected in August furnished 24·5 per cent. of dry substance. Sugar and starch, which were contained so largely in the root, could not be detected in the frond. The mode of treatment adopted by the author was the same as the above described.

The aqueous decoction was greenish-yellow, turbid and slightly acid; peracetate of iron produced a greenish precipitate of tannate of iron. Absolute alcohol threw down whitish-yellow flakes of gum. Tincture of iodine imparted a chocolate colour to it, arising from the tannic acid; no starch could be detected. Ammonia coloured the decoction reddish; acetate of lead produced a greenish-white precipitate, from which a mixture of æther and alcohol extracted chlorophyll. The treatment of the decoction with acids, with hydrate of magnesia and with recently precipitated carbonate and basic acetate of lead, afforded no peculiar organic substances. On distillation of the fronds, a trace of a volatile oil was obtained. The ætherial extract contained tannic acid and chlorophyll.

The alcoholic extract of the fronds, which had been previously exhausted with æther, was boiled with hydrate of magnesia to remove all tannic acid. The whole was then evaporated to dryness, and the small quantity of chlorophyll and alkaline chlorides again evaporated to dryness and exhausted with boiling water. The aqueous extract was mucilaginous, and had a feeble alkaline reaction, arising from dissolved magnesia. On evaporation, it left 22·2 grs. of a very viscous yellowish mass, readily soluble in water, from which it was precipitated by absolute alcohol. It was not

thrown down by acetic, hydrochloric or sulphuric acid; it furnished, with a solution of borax, a slight precipitate, which dissolved upon the addition of acetic acid. No precipitate was produced by perchloride and sulphate of iron. Acetate of lead and protonitrate of mercury caused caseous precipitates; silicate of potash merely rendered the solution turbid. From its not being precipitated by silicate of potash and thickened by a solution of borax, this substance is most closely related to the solid mucilaginous gum-mucilage. With tannic acid it forms a neutral compound, which is soluble in alcohol and in water; but when separated from the tannic acid, it is precipitated by alcohol. The extract obtained with absolute alcohol consists therefore of a peculiar mucilage, tannic acid, traces of chlorophyll and alkaline chlorides.

The fronds were now treated with cold and boiling water, with dilute acid and dilute caustic potash; and in this manner gum, salts and pectic acid obtained.

The determination of the ash furnished, for 1000 parts of the frond, 50·1 parts of ash.

1000 parts of the frond contain	4·7 ash contain
Trace of essential oil.	0·2 silica.
5 wax.	0·1 perphosphate of iron ($2F^2O^3 + 3PO^5$).
87 chlorophyll.	0·3 sulphate of lime.
110 tannic and gallic acids.	0·4 phosphate of lime ($CaO + PO^5$).
57 peculiar mucilage.	1·3 carbonate of lime.
54 albumen.	0·3 chloride of sodium.
35 pectine.	0·6 chloride of potassium.
50 salts.	1·5 carbonate of potash.
602 fibre and loss.	4·7
1000	

Root of Asplenium filix fœmina.—The aqueous decoction had an insipid astringent taste and an acid reaction; peracetate of iron produced in it a bluish-green precipitate of tannate of iron; acetate of lead and ammonia likewise indicated the presence of tannic acid. Tincture of iodine coloured it dark blue; after long standing the colour passed into violet, but a few drops of dilute acid restored the intense blue colour. Absolute alcohol precipitated gum.

In this case the author was likewise unable to detect alkaloids or any peculiar substance. In general the treatment of the root was similar to that above described, but the constituents did not agree in their properties with those found in the case of *Aspidium filix mas*. The resin had the consistence and colour of rosin, could be rubbed to powder, and became soft and viscous in boiling water. The alcoholic solution did not redden litmus-paper; ammonia added to it rendered it turbid; a spirituous solution of acetate of copper caused no turbidness; a spirituous solution of acetate of lead gave a copious precipitate. The resin was sparingly soluble in sulphuret of carbon, insoluble in alkaline carbonates and in ammonia even on the application of heat, and dissolved in caustic potash only on

boiling. No precipitate was produced in the potash solution by chloride of sodium. It dissolved readily in oil of turpentine. It belongs therefore to the non-acid slightly-electrical resins.

The fat oil had at first a faint peculiar odour, which was subsequently accompanied with a rancid one and a most nauseous taste; it caused a fat stain upon paper and had no action upon litmus-paper. It dissolves readily in æther, pretty easily in boiling absolute alcohol, but is almost insoluble in weak spirit; the specific gravity is the same as that of water; on being mixed with acid protonitrate of mercury, it became solid like wax. With fuming nitric acid of 1·5 spec. grav., it became perfectly solid; it consequently belongs to the non-siccative oils.

The essential oil resembles more closely that of *Aspid. fil. mas*, but it is of a paler colour. 1000 grs. of the root furnished 49·4 grs. of ash.

1000 parts of the dry root contain		3·68 ash contain	
0·2	essential oil.	0·2	silica.
12·0	fat oil.	0·3	sulphate of lime.
4·0	resin.	0·08	perphosphate of iron.
13·0	vegetable gelatine.	0·1	phosphate of lime.
20·0	gum.	1·2	carbonate of lime.
50·0	albumen.	0·1	chloride of sodium.
75·0	starch.	0·4	chloride of potassium.
40·0	pectine.	1·3	carbonate of potash.
119·0	tannic and gallic acids.	3·68	
15·0	amylaceous fibre.		
649·4	ash.		
02·4	fibre and loss.		
1000·0			

Archiv der Pharm., lxv. 257.

Red and Green Fires. *By* Dr. Böttger.

The mixture for *red fire* recommended by the author is 40 parts of nitrate of strontia, 13 parts of sulphur, 2 parts of lime-tree charcoal, with which is mixed, with a horn spatula, in order to avoid explosion, 5 parts of perfectly dry chlorate of potash. For *green fire*, 12 parts of dry nitrate of baryta, 4 parts sulphur and 5 parts of chlorate of potash are mixed with the same precaution.—*Kunst- und Gewerbe-Blatt. für Baiern*, 1851, p. 144.

ANALYTICAL CHEMISTRY.

On the Tests for determining the Value of Cinchona Barks. *By* Dr. A. Buchner.

The author draws the attention of druggists to the importance of ascertaining the amount of alkaloids in the barks, and the preference

which this method deserves, to all others which are founded upon external characters. He calls attention to the method of examination proposed by Wöhler, and finds it to answer its purpose completely when the requisite time can be given to it. The author has made numerous experiments with a view to discover a process which shall require far less time. This process, the value of which was tested upon several Cinchona barks, gave the following results:—

Cortex Cinchonæ Regius.—2 oz. of this bark, which exhibited all the characters of being genuine, were exhausted with 8 oz. of water to which 1 scruple of officinal dilute sulphuric acid had been added, the mixture kept for twenty hours at a temperature of 122° to 140° F., frequently agitated, and then brought upon a filter. The filtered liquid was perfectly clear, of a very pale yellow colour, and possessed an agreeable aromatic odour and an acid bitter taste. The residual powder was digested twice more from twenty to twenty-four hours at the same temperature with 8 to 9 oz. of water and a few drops of dilute sulphuric acid until the last filtrate was rendered but faintly turbid by ammonia. The whole of the extracts were united, and the alkaloid precipitated until a filtered sample was no longer rendered turbid by ammonia. The precipitated quinine was collected upon a filter, washed, pressed and dried. In the moist state it had a chocolate-brown colour; when dry, it was dark reddish-brown, and weighed 21 grs. There were therefore obtained 2·187 per cent. of coloured quinine; the time requisite for this process may be further shortened by boiling, instead of digesting at the above-mentioned temperature. 1 oz. of the powdered bark was boiled for half an hour with 12 oz. of water and $\frac{1}{2}$ a scruple of dilute sulphuric acid, and the residual powder washed out with about 4 oz. more hot water, and the filtered solution immediately precipitated with ammonia or carbonate of soda. The precipitate is washed with cold water, and dried between blotting-paper.

The author purified this coloured quinine. This operation however was accompanied by so great a loss, that, calculating the quantity in the bark from the quantity of pure quinine obtained, it would amount only to $\frac{1}{2}$ per cent. For the purpose of testing a bark as to its genuineness, it suffices merely to prepare the coloured quinine, and this method is then both quick and simple.

This method was applied to the examination of the barks of *Cinchona fusca, C. Huamalies, C. flava, C. Surinamensis* and *C. Brasiliensis.* The test is easily applied and decisive when the question to decide is whether the powder has been prepared from *C. regia, C. fusca* or *C. flava*, or from any false Cinchona barks. Yellow bark, exhausted with hot water to which a little sulphuric acid has been added, furnishes a pale yellow infusion of a peculiar aromatic odour, which on being mixed with an excess of ammonia, gives a copious reddish-brown precipitate, and the liquid at the same time assumes a beautiful red colour; red bark, on the other hand, furnishes a brownish-yellow or ochreous precipitate, and the infusion is coloured yellowish-

brown by the ammonia. The pale Carthagena bark likewise yields with water acidulated with sulphuric acid a pale sherry-coloured infusion, which also gives a chocolate-brown precipitate with ammonia, like the infusion of yellow bark; but the filtered ammoniacal liquid is not red, but of a darker yellow. Huamalies bark, exhausted in the same manner, furnishes a dark yellow infusion of a less aromatic odour than the yellow bark, and with ammonia an ochreous precipitate like the brown Huanuko bark; but the filtered ammoniacal liquid is not yellowish-brown, but red, almost like the infusion of *C. regia*. The false barks furnish with pure water and with water to which a little sulphuric acid has been added, much darker-coloured infusions than the genuine barks; they possess a more astringent taste, and furnish no alkaloid when mixed with ammonia until they have an alkaline reaction.

If it be desired to ascertain the amount of alkaloid more accurately than is possible according to the above method, the acid extracts must be concentrated as much as possible by evaporation; moreover, the alkaline liquids filtered from the precipitated alkaloids should be evaporated to dryness in order to remove from them the remainder of the quinine or cinchotine.

The alkaloids precipitated from the acid infusions of the barks by ammonia or carbonate of soda are, in every case, combinations of them with a humus-like cinchona colouring substance, which in the *C. regia* is a different one from that contained in the brown kinds of bark, and is present in variable quantity. This colouring matter may be very easily separated from the alkaloid by acetate of lead.

It may be assumed that 1 oz. of yellow bark, exhausted with 12 oz. of water and from $\frac{1}{2}$ to 1 scruple of dilute sulphuric acid, will furnish, on precipitation by ammonia, not less than 10 grs. or 2 per cent. of the weight of the bark of coloured quinine.

The brown or Huanuko bark gives, on being treated in the same manner, only from 8 to 9 grs. of coloured alkaloid, and frequently less. Besides cinchonine, it contains another alkaloid, which is soluble both in æther and in water containing soda, and which is not quinine, but most probably cinchotine.

1 oz. of the Huamalies, or rusty bark, furnished 7·5 grs., or 1·54 per cent. of coloured alkaloid; it is therefore one of the richer kinds, and most probably more active. However, no quinine could be detected in it; for the portion which was pretty soluble in water and æther, on being dissolved in chlorine-water, was not rendered green by ammonia; it may therefore be assumed as highly probable, that the Huamalies, like the Huanuko bark, contains cinchotine besides cinchonine.

Of the pale bark, *Cinchona flava*, 1 oz. furnished 6·35 grs. of coloured alkaloid, or 1·32 per cent.; but it differs very remarkably from the *C. regia*, not only by its external characters, but also from its containing no quinine; the alkaloid in this kind appears to consist for the greater part of cinchotine. From the large amount of alkaloid contained in it, it is probable that the *C. flava*, though not

to be compared with *C. regia*, should be counted among the most active of the barks.

The spurious barks, both the *Surinamensis* and the *Brasiliensis*, are easily distinguished from the genuine by their external characters as well as by the fact that they furnish with acidulated water reddish-brown or brownish-red, and not pale yellow infusions, from which no alkaloid is precipitated by ammonia or carbonate of soda; they consequently possess no greater pharmacological value than the barks of our willows, ash and horse-chestnut.—Buchner's *Repert.*, viii. p. 145.

On the Action of Baryta and Strontia before the Blowpipe.

TO THE EDITOR OF THE CHEMICAL GAZETTE.

Dear Sir,—A letter which appeared in your Journal of Nov. 1, 1850, by Professor Chapman, has only just been pointed out to me. He endeavours in his note to find fault with me for some observations I made relative to the blowpipe reactions of strontia, baryta, &c., because, as he states, they reflect more than indirectly upon the accuracy of a little test announced by him in one of your previous Journals. I never publish a result unless I am convinced of its truth from experiment; therefore I beg to state, through the medium of your valuable Journal, that the reactions I mentioned as belonging to strontia, baryta, &c., and their soluble and insoluble *artificial* salts, are perfectly correct. When equal parts of chloride of strontium and chloride of barium are mixed, dissolved and evaporated to dryness, the strontia reaction is obtained before the blowpipe; soda *prevents this reaction*, the characteristic yellow of the soda appearing.

Desiccated carbonate, phosphate and sulphate of strontia *do not colour the blowpipe flame.*

Yours respectfully,
Sheridan Muspratt, F.R.S.E., Dr. Phil., &c.

College of Chemistry, August 22, 1851.

On the Detection of Sulphur. *By* J. W. Bailey.

Dr. Playfair's beautiful salt, the nitroprusside of soda, is justly recommended by its discoverer as the most delicate of all tests for alkaline sulphurets*. An application of it which is very obvious, although not alluded to by Dr. Playfair, is to employ it not only as a direct test for alkaline sulphurets, but as an indirect one for sulphur in any of its compounds. Any substance containing sulphur will yield an alkaline sulphuret if heated with carbonate of soda, either with or without the addition of carbonaceous matter, according as a deoxidizing action is or is not required. The mag-

* See London, Edinburgh and Dublin Phil. Mag., vol. xxxvi. p. 208.

nificent purple which is then produced by the addition of the fused mass to a drop of the solution of the nitroprusside will at once prove the presence of sulphur. This reaction is so easily obtained and is so decisive, that the nitroprusside of soda must take its place among the most useful adjuncts to the blowpipe tests. By means of it the presence of sulphur in the smallest particles of coagulated albumen, horn, nails, feathers, mustard seed, &c., which can be conveniently supported on a platinum wire for blowpipe experiment, may be most distinctly shown; and I have repeatedly obtained the characteristic purple tint in operating upon a piece of a single fibre of the human hair *less than an inch in length.*—Silliman's *Journal*, May 1851.

PATENT.

Patent granted to Ewald Riepe, *for certain Improvements in refining Steel.*

This invention consists in refining raw or crude steel (particularly puddled steel), by placing bars or lumps thereof in a furnace or other heating chamber, where the atmospheric air cannot exert an injurious action upon it, and subjecting it therein, for a suitable time, to a temperature not exceeding that which will melt steel.

The patentee states, that he uses a welding furnace, such as is ordinarily employed in puddling iron, only that the bed is lowered, the grate is brought from 2 to 4 feet below the level of the fire-bridge, and the ash-pit is furnished with an iron door, by which it can be completely closed. When the furnace is in full heat, the bars or lumps of raw or crude steel are laid on the bed of the furnace, and arranged so that they may not touch each other at any part. During the whole of the refining process, the fireplace is kept fully charged with coal or other fuel; any crevices in the working-door, or elsewhere, are carefully luted with wet clay, in order t prevent as much as possible the access of oxygen; and the draught of the furnace is so regulated, by means of the ash-pit door and flue-damper, that the heat shall never reach the melting-point of steel. A sufficient practical test of the heat is furnished by the colour of the flame, which is watched through an eye-hole in the working door; as long as the flame remains of a dull or hardly red colour, the heat will not be greater than is requisite. From 900 to 1000 lbs. of raw or crude steel, in bars of 3 inches by $1\frac{1}{2}$, are usually placed in a furnace of the ordinary size, and the operation is continued for about four hours. In this process, carburetted hydrogen and oxide of carbon are produced in the furnace in abundance, while the oxygen of the air is effectually prevented from acting on the steel; and the product is steel of a very fine uniform grain.—Sealed Dec. 5, 1850.

THE CHEMICAL GAZETTE.

No. CCXVI.—October 15, 1851.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Volatile Acids of the Fatty Oil of the Spindle-Tree, Euonymus europæus. *By* Prof. E. Schweitzer.

The ripe seeds of the spindle-tree contain a large amount of a fat oil, which in various districts is expressed, and employed by the country people as a remedy against vermin in the hair of man and animals, and against old sores and wounds.

These properties led to the supposition that the oil contained some peculiar substances, and was submitted to examination in 1833 by Riederer. He found in it a resinous bitter substance, to which he gave the name euonymine, and a volatile fatty acid, which however he did not more closely examine. He procured it by saponifying the oil, and distilling the soap with phosphoric acid; but merely states that the aqueous solution had an acid reaction, and in other respects resembled the volatile oleic acid of *Croton Tiglium.*

The fatty oil of the spindle-tree is contained, according to Schweitzer, both in the seeds and in the orange-coloured perisperms. According to an observation of Nägeli, the pigment does not exist in the latter in a state of solution, but as a granular mass deposited on the cell-walls. On being submitted to pressure, however, the colouring matter dissolves in the oil, and imparts to it a brownish-yellow colour. The oil has a thickish consistence, a pale yellow colour in thin layers, a nauseous odour like rape-oil, and a bitter and subsequently pungent taste. It solidifies between 10° and 5° F., and the greater portion of the pigment likewise separates with the solid fat; but when the oil melts again, it does not entirely disappear, but adheres in the form of beautiful red granules to the sides of the glass. On agitating the oil with warm water, the latter acquires a bitter taste, but no colour. Riederer's statement, that water shaken with the oil turns blue litmus red, was not confirmed by the author. It is sparingly soluble in alcohol, readily in æther. A solution of the oil in a mixture of alcohol and æther gave no precipitate with an alcoholic solution of acetate of lead.

On saponifying the oil with potash, a beautiful yellow soap is obtained; the oleic acid obtained by decomposing this with hydrochloric acid, deposits after some time nodules of colourless margaric acid, whilst the fluid portion still remains brownish-yellow. The oil which the author employed for his experiments had only been expressed a few days previously.

After saponification, the author separated the brown-coloured ley

from the soap, neutralized it with sulphuric acid, and concentrated it as far as possible on the water-bath. The residual mass was then submitted to distillation on the sand-bath with an excess of dilute sulphuric acid. Towards the end of the operation, some crystals made their appearance in the neck of the retort. The distillate had a strong acid reaction, an acid acrid taste, and the odour of acetic acid. On being shaken with æther, the greater part was taken up by it, and could then be easily obtained in the concentrated state by distilling off the æther on the water-bath. In a second preparation, the mass obtained by evaporating the mother-ley, neutralized with sulphuric acid, was exhausted repeatedly with alcohol, and from the residue left by evaporating the united spirituous extracts, the volatile acid separated by distillation with sulphuric acid. As in this manner most of the sulphate of potash, which causes violent succussion, is removed, the distillation with sulphuric acid was more easily carried out to the end.

Subsequently the operation was simplified still more by mixing dilute sulphuric acid in excess with the evaporated neutralized mother-liquor, and then agitating the liquor repeatedly with æther. The æther removed nearly the whole of the volatile organic acid, while the other substances with the sulphuric acid were left in the aqueous solution.

In the soap separated by pressure from the ley, only a small quantity of volatile acid was contained.

After evaporating the ætherial solution obtained in each preparation of the acid, the latter was left as an oily liquid, of a pungent acid odour and acrid acid taste. On being mixed with a little water, it congealed for the greater part, with evolution of heat, into a crystalline brownish mass, which was purified by expressing the fluid parts, recrystallizing it repeatedly from boiling water, and after drying, submitting it to sublimation.

The substance so purified has all the properties of *benzoic acid*. Its silver salt consisted of 50·78 oxide of silver and 49·22 acid; the benzoate of silver contains, according to the formula $AgO,C^{14}H^5O^3$, 50·67 oxide of silver and 49·33 benzoic acid.

The liquid separated by pressure from the benzoic acid contained more of this acid, but consisted principally of a more volatile acid, with a stronger smell. A large portion of the dissolved benzoic acid separated in the cold; to remove the remainder from the liquid, it was saturated with carbonate of soda, concentrated by evaporation, mixed with some sulphuric acid, and the eliminated benzoic acid separated by filtration. The acid filtrate was again saturated with soda, evaporated to dryness, the residue distilled with concentrated phosphoric acid, and in this manner the second acid obtained pure in the concentrated state; it possessed all the properties of concentrated *acetic acid*; it had the same odour and taste, the same behaviour towards nitrate of silver, protoxide of mercury and neutral persalts of iron. Moreover, the soda salt, on being heated in a tube with arsenious acid, gave off the peculiar odour of alkarsine; its silver salt was found to consist of 69·14 oxide of silver

and 30·86 acid; the acetate of silver contains, according to the formula $AgO, C^4 H^3 O^3$, 69·48 oxide of silver and 30·52 acetic acid.

According to this investigation, therefore, the oil of the spindle-tree contains no peculiar volatile fat acid; but what Riederer took for such is a mixture of benzoic and acetic acids. The acrid taste of the mixture is caused by the benzoic acid, the odour by the acetic acid. The liquid obtained in the preparation from the ætherial solution is a concentrated solution of benzoic acid in acetic acid. When mixed with water, the acetic acid combines with it, and the greater portion of the benzoic acid separates, being much more insoluble in the dilute acid.

As to the state in which the two acids are contained in the oil of the spindle-tree, Riederer admits that the oily acid is at least partially combined with euonymine, the bitter principle contained in the oil. With respect to this bitter principle, Riederer did not procure it in a pure state; but his euonymine was, as already observed by Grundner, a mixture of the bitter principle with resinous colouring substance. When the oil is shaken with warm water, the latter, as above stated, acquires a bitter taste, without in the least becoming yellow. The author treated a considerable quantity of the oil with boiling water; and after it had sufficiently cleared, evaporated the aqueous solution on the water-bath to dryness. In this manner a small quantity of the bitter principle was obtained in the form of a scarcely-coloured extract. On submitting it to distillation with sulphuric acid, not a trace of acetic or benzoic acid was obtained; whence it is evident that these acids are not combined with the bitter principle in the oil. They must therefore be contained in the oil either in the free state or in combination with oxide of glyceryle.

Water which had been agitated for a long time with the recently-expressed oil had not the slightest acid reaction. The same was the case with the water which had been submitted to distillation with the oil; whilst, on the other hand, the alcoholic solution distinctly showed an acid reaction with test-paper. It is evident from this that the acetic acid cannot be in the free state; it must exist therefore in combination with oxide of glyceryle, forming a peculiar fat, *acetine*. Although no such compound has as yet been observed, still its existence is not surprising, as acetic acid is a member of the series of the fat acids, and is very closely related to butyric and valerianic acids, whose fats are well known.

The acid reaction of the alcoholic solution of the oil renders it probable, on the other hand, that the benzoic acid occurs in the free state merely dissolved in the oil; that in this case the water shaken with the oil acquires no acid reaction, may be explained from the great solubility of benzoic acid in fatty oils. This occurrence of benzoic acid appears not to be accidental, when we take into consideration the simultaneous production of acetic, butyric, valerianic, caproic and benzoic acids in the action of oxidizing agents upon the proteine compounds.

Experiments to separate, according to the above method, fatty acids and benzoic acid from other fat oils furnished a negative

result. A mere trace of acetic acid was obtained, which Chevreul also detected in small quantity in hog's lard.—*Proc. Nat. Gesells. Zurich*, 1851.

On the Deportment of Water towards Bases. *By* Prof. H. Rose.

When water plays the part of base, it can only act as a feeble one, and is consequently only capable of precipitating oxides of weak basic properties from their solutions.

Of the oxides, which consist of equal atoms of oxygen and metal, and which in general form powerful bases, only the peroxide of mercury and the protoxide of palladium are separated by water from solutions of their oxysalts, partly in the form of oxides and partly as basic salts. The corresponding chlorides are, on the contrary, not decomposed by water, just as, in fact, other weak bases are not capable of separating these oxides from their chlorine compounds. Protoxide of tin is eliminated by water from the protochloride, but not from that recently prepared.

Of those oxides which consist of 2 atoms of metal combined with 3 of oxygen, the majority are precipitated by water from their salts, several at the ordinary temperature, but some only on ebullition. A few only, for instance glucina and alumina, are not precipitated from their solutions in water either in the cold or at an elevated temperature. These oxides must therefore be regarded as the strongest bases of the group of oxides containing 2 atoms of metal to 3 of oxygen.

The oxides of bismuth and antimony are eliminated from their salts by water at the ordinary temperature in the form of basic salts; the same happens with arsenious acid when it occurs as base, and also with the oxide of manganese.

Peroxide of iron is precipitated from its solutions by water only on ebullition; the same is the case with the sesquioxide of cobalt from the acetic solution, the oxide of cerium and the oxide of uranium, but the latter only from the acetic solution and not from the nitrate.

Those oxides which contain 2 atoms of oxygen to 1 of metal behave in most cases as acids; but when they occur with basic properties, they belong to the weakest bases. Peroxide of tin, titanic acid and tellurous acid (oxide of tellurium) belong to this group; the latter is precipitated from solutions in acids by water even in the cold, but the former only on ebullition.

With respect to those oxides which contain 1 atom of oxygen to 2 of metal, they have frequently been regarded as very feeble bases; this however is a great mistake. They belong to the most powerful bases, and from their composition they must possess stronger basic properties than those oxides which consist of equal atoms of metal and of oxygen. To this group belong the suboxide of lead, the protoxide of copper, the protoxide of mercury and the protoxide of gold.

The basic properties of the suboxide of lead cannot be judged of,

as it is decomposed by all acids and by alkalies into metal and oxide of lead. The suboxide of lead therefore is not known as a base.

The basic properties of the protoxide of mercury are likewise difficult to determine, as it is impossible to test their power by means of other bases, from the protoxide being most readily resolved into metal and oxide even by very weak bases, whilst towards acids it acts as a decidedly powerful base, and forms a series of remarkable salts with strong and weak acids. Water also acts as a weak base, especially at a high temperature; and it is owing to the decomposition which the water produces as base, that the powerful basic properties of the protoxide of mercury have been entirely overlooked. But the protoxide of mercury is never precipitated by water from solutions of its neutral salts. Only from the crystallized basic protonitrate of mercury, which may be regarded as a double salt consisting of a still more basic one and of the neutral protonitrate, is the latter dissolved out by cold water, while the former is left behind undissolved.

It is far more easy to recognise the strong basic properties in another oxide, which possesses a similar composition to the protoxide of mercury and a similar deportment towards reagents,—the protoxide of copper. This is likewise decomposed by several reagents into oxide and metal, like the protoxide of mercury; but whilst in the case of the latter this takes place to a less extent when it is brought into contact with acids, while it is decomposed by bases even the most weak, the opposite occurs with the protoxide of copper, which resists decomposition by bases even when they possess strongly basic properties, but is decomposed by acids into metal and oxide. This is the reason why we do not possess such a series of remarkable salts as in the case of the protoxide of mercury. Hydrochloric acid dissolves the protoxide of copper without decomposition, or rather it converts it into protochloride of copper.

In the solution of the protochloride of copper in excess of hydrochloric acid, which may be regarded as a solution of the protoxide, the strongly basic properties of the protoxide of copper are easily recognised. It is true that the protochloride of copper is thrown down by water from this solution in the form of a white powder; but this acts as a base towards the hydrochloric acid, and neutralizes its acid properties. Strong bases, as hydrate of potash, produce the same effect as water when added in small quantity to the solution; it requires an excess to separate the protoxide of copper from the protochloride. But if chloride of sodium is mixed with a solution of the protochloride (with which it forms a very soluble double salt, the solution of which is not rendered turbid by water), no protoxide of copper is precipitated from it by carbonate of baryta. The mixture may even be heated somewhat without any protoxide being thrown down. Consequently the protoxide of copper must be classed with the powerful bases; it is a far stronger base than the peroxide of copper, which is separated from its solutions by carbonate of baryta even in the cold.

The basic properties of the protoxide of gold are very little known,

as it is insoluble in oxyacids; but that it cannot be a weak base follows from the constitution of the purple of Cassius, which is a double compound of the stannate of the protoxide of gold with the stannate of the oxide of tin.—*Bericht der Acad. zu Berlin*, 1851, p. 284.

On some Sulphocyanides. *By* John Hull.

The Per- and Protosulphocyanide of Copper, Cu^2, C^2NS^2+Cu, C^2NS^2.—The persulphocyanide of copper required for the preparation of this compound is most advantageously obtained, according to the author, by adding a slight excess of sulphuric acid to a moderately-concentrated solution of sulphocyanide of potassium (which has been freed from air by ebullition, and then allowed to cool), and directly afterwards a saturated solution of persulphate of copper free from air. The persulphocyanide of copper instantly separates as a black crystalline precipitate, which is quickly washed, and dried over sulphuric acid. It is decomposed by long contact with water, and immediately on being heated with it.

The persulphocyanide of copper dissolves with a brown colour in a concentrated aqueous solution of sulphocyanide of potassium. Water precipitates from this solution the protosulphocyanide of copper and the yellow double salt. This latter is obtained pure when the persulphocyanide is dissolved in a warm solution of sulphocyanide of potassium in alcohol, and evaporated at a gentle heat. It then separates, and even the still undissolved portion of the persulphocyanide is converted into this compound. It is collected on a filter, washed with alcohol, and lastly with water. It is apparently likewise formed when the persulphocyanide of copper is gently heated upon platinum foil over a spirit-lamp. A brownish-yellow spot forms where the temperature is highest, from whence the change extends rapidly through the whole mass, without ignition, but with evolution of sulphuret of carbon, cyanogen and other volatile products. The substance thus obtained is brownish-yellow, and behaves essentially like that above described.

The double sulphocyanide of copper forms a yellow amorphous powder, which is unalterable in water and insoluble in sulphocyanide of potassium. It contains no water. It is decomposed by solution of caustic potash, with production of sulphocyanide of potassium. Hydrochloric acid does not alter it even on the addition of chlorate of potash or on the application of heat. Concentrated nitric acid destroys it with violence, with formation of sulphuric acid. The compound, dried at 248° F., furnished on analysis—

Cu.....	45·28	3	= 44·95
C^2NS^2	53·62	2	55·05

Sulphocyanide of Potassium and Silver, K, C^2NS^2+Ag, C^2NS^2, is obtained by precipitating sulphocyanide of silver from a silver solution with sulphocyanide of potassium. If this be dissolved, with the assistance of heat, in a solution of sulphocyanide of potassium, this solution, if it has been saturated with it, deposits, on being set

aside over sulphuric acid, the sulphocyanide of potassium and silver in colourless right rhombic crystals, which are not altered by exposure to the air if the mother-liquor has been completely removed, have considerable lustre, and when rubbed become soft like the ferrocyanide of potassium. They are completely decomposed by water into sulphocyanide of potassium and crystalline sulphocyanide of silver. When this decomposition is observed under the microscope, by moistening a crystal with a drop of water, it is seen to break up into granules, which gradually assume the form of prisms. The compound fuses at 284° without decomposition. At a somewhat higher temperature it is decomposed with ebullition and turns black. When it has been heated for some time and the mass is then treated with water, there frequently remain long prisms of the sulphocyanide of silver. The compound, dried at 212°, furnished on analysis—

K	15·13	1	14·85
Ag.....	39·95	1	41·00
C^2NS^2	44·01	2	44·15

Recently-precipitated cyanide of silver, and likewise the chloride of silver, is readily dissolved by a concentrated solution of the sulphocyanide of potassium. Water precipitates crystalline sulphocyanide of silver from the solution.

On attempting to prepare definite compounds of the proto- or persulphocyanide of copper with sulphocyanide of potassium, the expected results were not obtained. The protosulphocyanide dissolves, it is true, pretty largely in a strong solution of the sulphocyanide of potassium, but no definite compound could be obtained from it. Water separates from the concentrated solution white protosulphocyanide of copper in a crystalline form.—Liebig's *Annalen*, lxxvi. p. 93.

On the Action of a red Heat upon Alcohol and Acetic Acid.

By M. Berthelot.

The vapour of alcohol, passed through a porcelain tube filled with pumice-stone and heated to redness, yields carbon, gaseous hydrocarbons, aldehyde, naphthaline, benzine, phenic acid, and various other substances.

The naphthaline is obtained in a crystalline state. I determined its melting-point. It had previously been noticed in the decomposition of alcohol by Saussure and by Reichenbach, and in that of the Dutch liquid by M. Regnault.

The presence of benzine may be proved by passing the gases into fuming nitric acid, and then precipitating by water. The substance thrown down has a decided odour of bitter almonds, which is possessed by nitrobenzine; with nascent hydrogen it yields a mixture of naphthalidame and aniline. The aniline was proved to be present by means of chloride of lime, which gives rise to the characteristic violet colour.

Lastly, with the naphthaline, which it constantly accompanies, a volatile oil condenses, which disorganizes the skin, dissolves in water and in æther, combines with soda, and furnishes picric acid on treatment with nitric acid. This oil appears to be phenic acid.

When the vapour of acetic acid is submitted to the same treatment, only a small portion is destroyed, with the production of carbon, combustible gases, acetone, naphthaline, phenic acid, benzine, &c.

It results from these facts, that, by distilling through a tube at a red heat substances whose equivalents are not very high, as alcohol and acetic acid, the same hydrocarbons, and the same stable substances, so little alterable by heat, are produced as we obtain in the distillation of such complex substances as coal and the fatty oils. These substances appear therefore to be the constant and essential products of every distillation at a red heat of a non-nitrogenous organic matter. These products are developed in virtue of a peculiar affinity—a special molecular complication. Their formula does not appear to be connected by a simple derivation with that of the decomposed matter. Their presence does not require the identity in all cases of the substances distilled; thus the decomposition of acetic acid and that of alcohol present a totally different physiognomy. They are essential, but not dominant products.

The experiments relative to acetic acid lead to another very curious conclusion; it is that the synthesis of these substances, naphthaline, benzine, and probably phenic acid, or rather the possibility of reproducing them, starting from the simple bodies of which they are constituted, should be regarded as an accomplished fact. They are, in fact, obtained by means of acetic acid. At the present day we are able to produce acetic acid by several processes; I will merely mention one, the reaction by means of which M. Kolbe passes from the sulphuret to the chloride of carbon, then to chloracetic acid; which latter, as is well known, on being treated with potassium amalgam, was found by M. Melsens to reproduce acetic acid.—*Comptes Rendus*, August 18, 1851.

Observations on White Precipitate. *By* Dr. R. Wagner.

Sir Robert Kane assigned the formula $HgCl, NH^2Hg$ to the officinal white precipitate, and considers this substance as a combination of 1 equiv. perchloride of mercury with amidide of mercury.

Gerhardt and Wurtz have rendered it probable that the so-called platinum bases are ammonias in which different amounts of hydrogen are replaced by platinum. Similar views are entertained by Wurtz respecting the composition of the base cupramine, N^2CuH^5, which he supposes to exist in the so-called ammonio-chloride of copper.

If we extend the views of Gerhardt and Wurtz also to the above-mentioned amidogen compound of mercury, it becomes a combination of perchloride of mercury with mercuramine, *i. e.* with ammonia in which 1 equiv. hydrogen is replaced by 1 equiv. mercury, $HgCl + NHgHH$.

Whether the preceding formula is the rational one for white precipitate can be ascertained in the following manner:—If mercury replaces the hydrogen of the ammonia, it must admit of being removed and replaced by 1 equiv. of an alcohol radical, for instance by æthyle, amyle, &c. If the amidide of mercury can be converted into æthylamine, amylamine, &c., we have a proof that the first-mentioned substance is the ammonia base mercuramine.

The author mixed dried white precipitate with amylic mercaptan; mercaptide was formed, with the evolution of a considerable quantity of heat, so that a loss of mercaptan could not be avoided. The most advantageous method was to suspend the white precipitate in water, and then to add the mercaptan, in very small proportions at a time, until the odour of the latter no longer disappeared. The white amorphous substance thus obtained was dried at 212°, and then submitted to distillation in a small retort at a gradually increasing temperature. Black sulphuret of mercury was immediately formed; and at first a liquid passed over, which smelled of ammonia and amyle. Subsequently a deposit resembling sal-ammoniac was formed in the neck of the retort. The neck of the retort was washed out with hot water, and the filtered solution mixed with the liquid which had passed over. Some metallic mercury was found in the upper part of the retort. The liquid had a decided odour of amylamine and an alkaline reaction. It was saturated with hydrochloric acid, evaporated on the water-bath, and precipitated by chloride of platinum with the addition of alcohol. The double salt is of a golden colour, and is seen to consist, under the microscope, of distinct regular octohedra. It contains 33·9 per cent. metallic platinum. The formula $C^{10}H^{11}H^2N, ClH + PtCl^2$ requires 33·3 per cent.

When heated with a solution of potash, the platinum double salt disengages the characteristic odour of amylamine. Although the white precipitate employed had been dried, it nevertheless contained some water, which must have given rise to the formation of a small quantity of the ammonia. This explains the too large amount of platinum in the analysis of the double salt.

Leaving out of consideration the collateral products formed in the action of amylic mercaptan on white precipitate, the production of the muriate of amylamine may be expressed by the following equations:—

$$1.\ \left.\begin{matrix}Hg\\H^2\end{matrix}\right\}N, HgCl, \text{white precipitate} + C^{10}H^{11}S, SH, \text{amylic mercaptan}$$
$$= C^{10}H^{11}S, HS, \text{amylic mercaptide} + \left.\begin{matrix}Hg\\H^2\end{matrix}\right\}N, ClH.$$

2. On the application of heat, the two last-mentioned compounds split up into

$$2HgS + C^{10}\left.\begin{matrix}H^{11}\\H^2\end{matrix}\right\}N, ClH.$$

The collateral products which originate in the formation of the

amylamine cause a great loss of mercaptan. The platinum double salt of amylamine is partly decomposed by long-continued boiling, with separation of fusel oil.

As in the preceding experiment amylamine, and not diamylamine, was formed, the formula of white precipitate appears to be—

$$\left.\begin{matrix}Hg\\H\\H\end{matrix}\right\}N, HgCl, \text{ and not } \left.\begin{matrix}Hg\\Hg\\H\end{matrix}\right\}N, ClH;$$

for if the last formula were the rational one, which supposition however is opposed to the behaviour of white precipitate towards reagents, then on treatment with amylic mercaptan, diamylamine ought to have been formed.

It may perhaps prove possible by an nalogous treatment, to ascertain the constitution of the so-called metallic nitrurets. The nitruret of mercury is, for instance, NHg^3. Now if this be ammonia in which all the hydrogen has been replaced by mercury, then on treatment with sulphæthyle it should furnish sulphuret of mercury and triæthylamine. It is certainly remarkable that in the nitrurets the nitrogen is to the metal in the proportion of 1 : 3, 2 : 3 and 1 : 6. It will also be possible to ascertain, by a similar treatment, whether the fulminates contain nitrurets or not.—*Journ. für Prakt. Chem.*, liii. p. 378.

CHEMISTRY APPLIED TO ARTS AND MANUFACTURES.

On the Composition of the Substances employed by the Chinese in the Manufacture of Porcelain. By MM. Ebelmen *and* Salvetat.

The authors have analysed a series of substances, collected in China by a resident Catholic priest, Father Ly, which there form the material for the manufacture of porcelain. Some other substances, which are especially used for decoration, were brought from Canton by M. Itier. It results from this investigation that—

1. The kaolins and the *Pe-tun-tse* of the Chinese completely resemble the substances employed by the Europeans for the same purpose. The Chinese kaolins have undoubtedly originated from the decomposition and disintegration of granite rocks. The pe-tun-tse is identical in its mineralogical properties with compact felspar or hornstone, and resembles the pegmatite of Limosin. The pe-tun-tse consists of hornstone reduced to a fine powder, and formed into cakes, which together with the kaolins give the porcelain mass.

2. It appears that the mechanical arrangements for the production of the pastes are the same as with us.

3. The Chinese porcelain clays are more readily fusible than the European, and the same is the case with the Chinese glazes.

The greater fusibility and the greenish colour of the Chinese porcelain appears to be owing to an addition of lime to the pe-tun-tse. The pe-tun-tse alone might perhaps serve as a glaze for the porcelain manufactured in France. The Chinese porcelains have been generally considered as peculiarly hard, but they are certainly baked at far lower temperatures than those at Sèvres and Meissen; they are harder than the porcelains with lead-glaze. All the following analyses and statements refer merely to the manufacture of porcelain at King-te-tching in Kaiang-si, at which place there are, according to d'Entrecolles, more than 3000 porcelain furnaces and a population of 100,000. Father Ly gives the following account of the manufacture of the porcelain:—

"All the materials employed in the manufacture of porcelain in China are stones which are dug out of the soil or from rocks, with the exception of the *kao-ling* from Tong-kang and from Sy-kang, which are sands; they are suspended in water, in order to obtain the finest powder. All the stones are ground to powder, then diffused in water, in which they are stirred with a rod, and the upper layers of the water drawn off; these deposit the mineral in an exceedingly fine state of division, of which the pastes are formed. All the pastes are brought to King-te-ching into the houses of the workmen, who diffuse them again in water, pass the masses through sieves, dry the sediment somewhat, and then work it. The materials do not occur together in one spot in China; some are brought from very distant places. Some come from Khy-men-hien, others from Fou-leang-hien, others from Yu-kan-hien, and even from the province Hou-pe, as for instance the *chy-kao*. At King-te-ching all the finely-worked materials and pastes can be bought; but it is frequently necessary to search far and wide in order to procure the raw materials. I have succeeded in obtaining twelve different materials, of which however neither one alone furnishes porcelain. The workmen told me, some of the materials furnished the bone for the porcelain; this is the case with the *kao-lings* from Tong-kang and Sy-kang; others yield the body for the porcelain, as the masses from San-pao-p'ong, from Yu-kan-hien, &c. If the vessels be formed merely from kao-ling, they crack in the fire, because the kao-ling is too hard; if they are made from the other materials without kao-ling, they dissolve in the fire (like flowers which fade in the heat of the sun), because their nature is too weak, and they cannot stand twenty-four hours' fire. I distinguish four kinds of porcelain. To prepare the first, or best kind, 1 lb. of kao-ling is mixed with 2 lbs. of material from Khy-men; for the second, 4 lbs. *say-pe* from Tong-kang and 2 lbs. of *kao-ling* from Sy-kang; for the third, 2 lbs. of material from San-pao-p'ong and 1 lb. of *kao-ling* from Tong-kang; for the fourth kind, 1 lb. of material from Yu-kan-hien with 1 lb. of *hoa-chy* and 1 lb. of *kao-ling* from Sy-kang."

It is quite evident from this letter, that the Chinese, in their

manufacture of porcelain, proceed exactly in the same way as we do. They dig up and lævigate the kaolins, the substances from Tong-kang and Sy-kang, and mix them with finely-pulverized and lævigated quartz and felspar-sand.

Kaolin *from Tong-kang, Province Fou-leang-hieng.*—The crude kaolin furnished by elutriation, 43 per cent. of clay dried between 95° and 104° F., does not effervesce with acids, and resembles the kaolin of St. Yrieix, which is used at Sèvres; it does not fuse in the porcelain furnace, but contracts very much. The residue distinctly shows it to originate from a granitic rock, probably from pegmatite.

Kaolin *from Sy-kang, Province Fou-leang-hieng.*—This contains a very large amount of quartz, and furnishes on elutriation only 7 per cent. of clay. The residue consists in quartz granules and partially-decomposed crystals of a rose-coloured felspar and golden mica.

The following table of the analyses show the relation of the constituents compared with those of the clay of St. Yrieix. The analyses are made with the washed out clay:—

	Kaolin from Tong-kang,	from St. Yrieix,	from Sy-kang.	Quartzose kaolin from St. Yrieix.
Water	11·2	12·62	8·2	7·2
Silica	50·5	48·37	55·3	56·9
Alumina	33·7	34·95	30·3	31·6
Peroxide of iron	1·8	1·26	2·0	0·5
Magnesia	0·8	traces	0·4	
Lime	..	..	..	0·5
Potash	1·9	2·40	1·1	3·4
Soda	..		2·7	
Loss	0·1	0·40		
	100·0	100·00	100·0	100·1

The great similarity of the Chinese kaolins to those of St. Yrieix is sufficiently evident from these analyses. The French kinds are obtained from decomposed layers of pegmatite, in the neighbourhood of which both hard and partially kaolinized felspathic rock occur. The Chinese kaolins undoubtedly originate from granite.

In the following tables are arranged together the results of the analyses of those substances, which, according to the expression of the Chinese workmen, constitute the body of the porcelain. The above kaolins, which impart to the porcelain its infusibility in the fire, they look upon as the bone of the porcelain; all those rocks, which, on the contrary, serve to produce the requisite fusibility of the kaolins and the translucency of the porcelain, are termed the body of the porcelain; they are all of them hornstone, of a conchoidal or splintery fracture, with the hardness peculiar to this mineral. The analyses, so far as it was possible, were made with the same rock in the crude and in the prepared state. The following are the results:—

	Khy-men-hien.		San-pao-p'ong.		Siao-ly.	
	1. Crude material.	1*. Prepared.	2. Crude material.	2*. Prepared.	3. Crude material.	3*. Prepared.
Loss in the fire	2·94	3·05	3·10	3·05	3·76	3·25
Silica	76·20	76·26	74·90	75·00	76·30	76·41
Alumina	13·60	14·20	14·00	14·15	13·15	13·90
Peroxide of iron	traces	traces	0·80	0·10	0·85	0·90
Oxide of manganese	traces	0·35	0·20	traces	0·30	traces
Lime	0·12	traces	traces	0·12	traces	0·35
Magnesia	traces	traces	traces	0·15	traces	traces
Potash	3·28	3·00	3·00	3·10	3·10	3·00
Soda	5·05	4·00	3·90	3·04	2·17	2·50
	101·19	100·86	99·90	98·71	99·53	100·31

	Yu-kan-hien.			Say-pe.	
	4. Crude material.	4*. Prepared.	4†. Prepared.	5. Crude material.	5*. Prepared.
Loss in the fire	2·40	2·40	2·60	2·00	2·50
Silica	74·70	77·00	74·40	75·40	73·60
Alumina	15·90	15·70	15·00	16·00	17·80
Peroxide of iron	..	..	traces	0·10	
Oxide of manganese	0·10	..	..	traces	traces
Lime	0·10	0·20	0·10	0·40	0·50
Magnesia	0·20	..	..	traces	0·10
Potash Soda	6·40	4·70	6·90	6·00	5·50
	99·80	100·00	99·00	99·90	100·00

The external properties of these rocks, the analyses of which are given in the preceding tables, are as follows:—

1. *Rock from Khy-men-hien.*—Large fragments of a grayish-white rock, of a conchoidal and scaly fracture, spec. grav. 2·64, containing interspersed crystals of quartz, and fusing before the blowpipe into a white enamel; the pieces are coated with dendritic figures of oxide of manganese.

This material is likewise employed by the Chinese as a glaze; a piece of porcelain, coated with it, and baked in the usual way at Sèvres, acquired a beautiful glaze. Its composition is very similar to that of pegmatite, which is used for glaze in France; the powder obtained by lævigation had the spec. grav. 2·597, and the following composition:—

Water	0·40
Silica	76·10
Alumina	15·37
Peroxide of iron	0·13
Lime	0·17
Magnesia	traces
Potash	2·84
Soda	4·58
Loss	0·41
	100·00

2. *Rock from San-pao-p'ong in Fou-leang-hien.*—This is of a gray colour, with a splintery fracture, and exhibits, like the preceding one, dendritic figures of oxide of manganese on the fracture. It appears to be somewhat less fusible than the preceding one.

3. *Rock from Siao-ly in Fou-leang-hien.*—A greenish hornstone, with a splintery fracture, and the spec. grav. 2·66.

Some scales of white mica are perceptible in it, and at some places little cubes of iron pyrites. It fuses, like the preceding rock, in the fire of the porcelain furnace.

4. *Material from Yu-kan-hien.*—A grayish rock, with a splintery uneven fracture, with some reddish veins; spec. grav. 2·64; fusibility and appearance nearly like the preceding.

All those numbers with a * are the prepared materials of the same number; 4†, a pulverized mixture of rock from Khy-men and rock from Yu-kan-hien, completely prepared.

5. *Rock from Say-pe in Tong-kang.*—A greenish hornstone, with a conchoidal and splintery fracture; contains some crystals of iron pyrites; spec. grav. 2·64; and closely resembles the hornstone from Siao-ly (3.); its fusibility appears also to be about the same.

It is remarkable that the Chinese hornstone contains a perceptible amount of water, which is not expelled at 212°.

Hoa-chy.—The substances comprised under this name exhibit the greatest differences according to the localities whence obtained. The authors have examined three kinds; the first is from the collection of Father Ly, the second from the Sèvres collection, and the third was procured from M. Itier.

I. *Hoa-chy from Ngan-jing-hien.*—That sent by Father Ly is dug out from the soil and lævigated; according to his statement, it furnishes the inferior quality of porcelain clays when mixed with the above analysed hornstones and kaolins, and it likewise differs from all hitherto known. In the Sèvres collection there are two samples; one consists of the elutriated clay, the other forms the residue; the first is soft to the touch, has a somewhat yellow colour, and does not effervesce with acids; the other consists of agglomerated pieces, of the same colour as the clay, mixed with a large number of coarse crystalline particles of quartz.

In the collection of the Ecole des Mines, the authors found the rock which probably furnishes the hoa-chy on its decomposition; it is labelled "*Rock from the Mountains of Ngan-jing-lao-chan,*" and is a yellow crumbling mass, in which is seen a large number of bipyramidal crystals of quartz. This rock is therefore not a sedimentary one, but a quartzose porphyry. Analysis I. is that of the clayey portion, II. of the sandy portion in the Sèvres collection, III. that of the mineral from the Ecole des Mines. Its difference in composition is owing to its being in a less advanced state of disintegration:—

	I. Clayey portion.	II. Sandy portion.	III.
Water (loss in the fire)..	9·0	2·9	5·00
Silica	65·0	85·0	70·00
Alumina	22·3	9·2	20·95
Peroxide of iron	2·5	0·6	0·80
Lime	traces	..	traces
Magnesia	traces	traces	traces
Alkalies and loss	1·2	2·3	
Potash	..	..	3·20
Soda	..	..	0·90
	100·0	100·0	100·85

II. *Hoa-chy from Koansi* has been placed among the serpentine rocks by Brongniart. According to the examination of the authors, it does not belong there; its composition rather resembles that of halloysite, from which it essentially differs only in the amount of water. Two samples, I. hoa-chy from Koan-sy, II. hoa-chy from Su-chu-en, furnished on analysis—

	I. Hoa-chy from Koan-sy.	II. Hoa-chy from Su-chu-en.
Loss in the fire ..	16·50	16·50	15·52
Silica	48·00	44·00	45·00
Alumina	32·00	38·50	37·10
Peroxide of iron..	traces	traces	1·20
Lime	traces	traces	traces
Magnesia	2·50	1·40	2·10
Alkalies	1·00	0·64	0·52
	100·00	101·04	101·44

III. *Hoa-chy from Oia-tsia*, sent by M. Itier, consists of large radiate fragments, of a fibrous texture, and with a white fracture. The fibrous nuclei have all the external properties of tremolite; interiorly they are combined with a very soft substance, which appears to be soapstone; the fibrous portion however is by far the most predominant. On being treated with hydrochloric acid, a violent disengagement of carbonic acid results, and the liquid contains lime and magnesia. Its specific gravity is 2·90; it is undoubtedly a mixture of white amphibole with hydrated trisilicate of magnesia, of which soapstone is composed. In the hoa-chy which has not been purified, this mixture occurs together with a certain quantity of dolomite, the amount of which however appears to be variable. According to Beudant, the specific gravity of tremolite is 2·9–3·15, that of steatite 2·6–2·8. This hoa-chy does not fuse nor soften in the porcelain furnace; it becomes very hard in it, and after the baking scratches glass. On analysis it furnished—

		Oxygen.
Loss in the fire	1·27	
Silica	60·79	32·26
Lime	10·25	2·29
Magnesia	26·50	10·26
Alumina and iron	0·40	
	99·21	

Prepared Materials.—The following analyses relate to the pastes prepared by the Chinese, and forwarded by Father Ly, and which on baking furnish the Chinese porcelain. This gentleman collected several mixtures for porcelain of different qualities. Of the following three kinds of best and better quality, experiments which were made in the furnaces at Sèvres have shown that the difference in the quality of these three masses is due to the more or less yellow colour which they acquire in the baking. The mass of the first quality burnt very white, whilst the last sample after the baking was perceptibly yellow.

First Quality (labelled *B. a.*).—This mass is yellowish-white, loses water on calcination, and is partially decolorized; in the porcelain furnaces of Sèvres it burnt perfectly white. It does not effervesce on treatment with acids; hydrochloric acid deprives it of a small quantity of peroxide of iron and alumina, with a trace of manganese. It gave on analysis—

	Crude mass.	Material supposed to have been calcined.
Water	7·7	
Silica	63·6	69·6
Alumina	21·8	23·6
Peroxide of iron	1·1	1·2
Lime	0·3	0·3
Magnesia	0·2	0·2
Oxide of manganese	0·1	0·1
Potash	3·0	3·3
Soda	2·8	2·9
	100·6	100·6

It is highly probable from this analysis that the mass is a mixture of equal parts of chert from Khy-men-hien and kaolin from Tong-kang. The calculation then gives the following composition:—

Water	7·7
Silica	63·4
Alumina	22·7
Peroxide of iron, Lime, Magnesia	1·1
Potash	2·6
Soda	2·5
	100·0

Mass of Second Quality (labelled *B. c.*).—It consists, according to Ly's statement, of 2 lbs. of material from Khy-men, 4 lbs. of say-pe from Tong-kang and 2 lbs. of kaolin from Sy-kang, mixed with 2 lbs. of the mass from San-pao-p'ong or Siao-ly. It is probable that the information which Father Ly gives was obtained from a source which is not trustworthy. According to these statements, the kaolin could only constitute 20 per cent. of the mixture, which would not be very plastic, as the kaolin from Sy-kang contains a large amount of quartz. The analysis gave—

	Crude paste.	Supposed to be baked.
Water	7·05	
Silica	65·88	70·0
Alumina	20·88	22·2
Peroxide of iron	1·24	1·3
Lime	0·72	0·8
Magnesia	traces	traces
Potash	3·36	3·6
Soda	2·54	2·7
	101·67	100·6

Third Quality (labelled *B. i.*).—This mass is said to be formed of 2 lbs. of paste from Sang-pao-p'ong, 1 lb. kaoling from Tong-kang, or of 2 lbs. of material from Yu-kang with 1 lb. kaoling from Sy-kang, or with 1 lb. say-pe or mixture from Hoa-chy. The analysis furnished—

	Crude paste.	Supposed to be baked.
Water	6·7	
Silica	68·7	73·3
Alumina	18·1	19·3
Peroxide of iron	1·8	2·0
Lime	6·6	0·6
Magnesia	traces	
Potash	2·4	2·5
Soda	2·2	2·3
	100·5	100·0

The articles manufactured from 1 were very neatly worked, translucent, with a bluish tint; those from 2 were thicker, more blue and less translucent; those from 3 were of a coarse shape, very heavy, scarcely translucent, and with the glaze full of holes.

Pastes for the ordinary Porcelains (labelled *B. o.*).—According to Ly, these are prepared from the residues of the several kinds of pastes, and kaolin from Sy-kang. Their composition is—

	Crude paste.	Paste freed from water.
Water	9·25	
Silica	62·80	68·94
Alumina	19·41	21·30
Peroxide of iron	3·12	3·42
Lime	1·04	1·14
Magnesia	traces	traces
Potash	3·12	3·42
Soda	1·72	1·78
	100·46	100·00

The objects manufactured with it are translucent, but rather deserve the name of stoneware than porcelain. The shape is very crude, the glaze not uniform and with holes, the mass coarse and badly ground.

Glazes.—According to Ly, the basis of the glaze is *yeou-ko*, that is enamel. This enamel is employed for glazing all porcelains; it is a mineral, which is taken from the rocks of Tong-kang, Fou-keang-hien, and is prepared in the same manner as the rock from Khy-men. This yeou-ko is, according to the authors, likewise a hornstone, and related to those the analyses of which have been given above. A sample at the Museum at Sèvres forms a greenish rock with laminar fracture, in which are distributed some crystals of iron pyrites; spec. grav. 2·62. It fuses before the blowpipe to a white enamel. Employed as a glaze on the hard porcelain of Sèvres, it furnished satisfactory results, which were similar to those from Khy-men-hien. The following is the composition of the substance in the crude state, and as prepared by pulverization and elutriation:—

	Crude mineral.	Prepared mineral.
Water	2·7	2·3
Silica	75·9	75·9
Alumina	13·9	14·2
Peroxide of iron	0·7	0·8
Lime	0·4	0·5
Oxide of manganese	traces	0·3
Magnesia	traces	traces
Potash	2·9	2·8
Soda	3·8	3·5
	100·3	100·3

The yeou-ko, or enamel of the Chinese, which is well adapted as glaze for the hard porcelain of Sèvres, is not sufficiently fusible for the Chinese, on which account they mix it with lime, and probably also with the ashes of plants. Father Ly writes that the herb *langtchy* is common everywhere in China. A heap is made of alternate layers of this herb and lime, which is then fired; after the burning of the lime, the whole is mixed, treated with water to cleanse it and remove the coarse particles, and finally mixed with yeou-ko. The plants employed are ferns; they leave 0·049 of a reddish ash, which has the following composition:—

Soluble substances	19·5
Silica	64·5
Alumina, peroxide of iron, phosphate of lime	16·0
	100·0

The calcined lime which the authors examined contained a mere trace of substances insoluble in muriatic acid, and was for the greater portion converted into carbonate, but still turned litmus blue. The mixture of this lime with the ashes of the fern is called *yeou-hoe*; it contains only 4 per cent. of a residue insoluble in acids, and 94 per cent. of lime and carbonic acid. As the authors had no prepared glaze at their disposal, which would enable them to determine in what proportion the yeou-hoe was mixed with yeou-ko to prepare

the glaze, they analysed the glaze of two Chinese porcelain plates, and found—

Silica	68·0	64·1
Alumina	12·0	10·2
Peroxide of iron	traces	traces
Lime	14·0	21·0
Potash and soda	6·0	5·1
	100·0	100·4

According to this, the amount of calcareous substance mixed with the hornstone is very considerable. To this large amount of lime is owing the ready fusibility of the glaze, and likewise the more or less distinctly blue colour shown by the glaze of the Chinese porcelain. It had already been observed, that, by the addition of lime to the glaze of the hard porcelain of Sèvres, a decidedly greenish-blue colour resulted.

Chy-kao.—A mixture sent under this name by Father Ly is a beautiful white fibrous gypsum, containing 21 per cent. of water. According to Ly, this gypsum is a very necessary ingredient to the Chinese for the preparation of their mixtures. According to him, it comes from the mountains of Yu-tchheng-hien, in the province Hou-pe, and is used as an addition in the preparation of the masses, excepting the pastes formed of the kaolin from Tong-kong and Sy-kang, because the powder of all these substances will not form pastes without chy-kao. It is employed in the following manner:—In the first place, the powder of the substances is mixed with water, then some chy-kao powder added, and the whole stirred with a rod. After some time the powder subsides, and the water becomes clear. Before the grinding, the chy-kao is placed in the fire, to burn it somewhat; its action however is always the same, whether burnt or not.

The authors observe, that the Chinese at Pekin, in order to render yellow turbid water clear, dip a crystal of alum into it, when all the turbidity is soon precipitated. In the above process the gypsum undoubtedly acts likewise only mechanically, facilitating the subsidence of the suspended particles, as it was not again met with either in the composition of the glazes or the pastes.

In general the paste of the Chinese porcelain constantly contains more silica and alkalies than that of the European porcelain, and it is far more fusible. Cups from China became soft, and sunk entirely together in the furnaces used for the hard porcelain of Sèvres.

In conclusion, it is worthy of remark, that the Chinese have found that prepared pastes which have long been kept moist furnish the best porcelain; they are said to use mixtures which have been kept moist for a century. Supposing this to be true, it would be owing to the decomposition of the felspar ingredients.—*Ann. de Chim. et de Phys.*, vol. xxxi. p. 257.

PATENT.

Patent granted to William Stones, *for Improvements in the Manufacture of Safety-paper for Bankers' Cheques, Bills of Exchange, and other like purposes.*

The object of this invention is to manufacture a paper that will indicate, by discoloration of its surface, when an attempt has been made to extract written characters therefrom; and thereby to afford to bankers, merchants, and others, protection against forgery, or the tampering with cheques, bills of exchange, and other important documents.

The invention consists in the employment of iodine or bromine, together with ferrocyanide or ferricyanide of potassium and starch, either in the manufacture or preparation of safety-paper. For this purpose, iodine or bromine is used, in any of their ordinary combinations, with bases; but iodine being the cheaper material, is preferred to any compound of bromine. Of the compounds of iodine, the patentee employs in preference that known as iodide of potassium, such substance being the most readily attainable in the market, and in no degree affecting the colour of the paper. The mode of applying this substance is by mixing it with the pulp or size, or the paper may be saturated with a solution of the metallic iodide. The ferrocyanide or ferricyanide of potassium is mixed with the size, or it may be applied subsequently to the sizing, as in the case of the metallic iodide. The starch is preferred to be mixed with the pulp in the engine; but it may, like the other chemical ingredients, be used in an after-stage of the process.

The proportions for these several materials, used for rendering paper sensitive to the action of reagents, are by no means absolute; but as a guide it may be stated that the following have been found to answer the purpose, viz. for a ream of post weighing about 18 lbs.—

1 oz. iodide (or bromide) of potassium,
$\frac{1}{4}$ oz. ferrocyanide (or ferricyanide) of potassium,
1 lb. starch.

On the application to paper, prepared as above set forth, of reagents, to dissolve out or absorb any ink-markings therefrom, the tendency will be to break up one of the salts named. Thus, on the application of chlorine or mineral acids, the iodine will be liberated, and, combining with the starch, will form an insoluble iodide of starch of a dark colour; and, further, the iron which ink generally contains being attempted to be dissolved by either vegetable or mineral acids, the ferrocyanide of potassium will combine with it in solution, and form the well-known prussian-blue compound, which will become diffused over the adjacent portion of the paper.—Sealed Feb. 24, 1851.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Constitution of the Atmosphere. *By* B. Lewy.

The memoir which I have the honour to submit to the Academy contains the results of a series of researches on the constitution of the atmosphere, executed between France and New Granada, and from the coast up to 3193 metres above the level of the sea.

The analyses were performed by the new process of MM. Regnault and Reiset, which consists, as is well known, in analysing the air by volumes. To measure the elastic forces of the gas, I employed an excellent cathetometer constructed by M. Perraux; the process thus combined enables us to obtain much greater precision than has hitherto been reached in this class of experiments. To judge of the degree of accuracy attainable, it suffices to examine the numerical details of two analyses; and it will be seen that the greatest difference between two analyses made with the same sample of air never exceeded $\frac{1}{10,000}$th, and most frequently was not more than $\frac{1}{100,000}$th.

The various samples of air which I analysed were collected in bulb-tubes with the two ends drawn out and open; the capacity of these tubes was about 100 cub. centims. The air was collected in the following manner:—One of the extremities of the tube was connected, by means of caoutchouc tubing, with a little pair of bellows, which was moved sufficiently long to be certain that the whole of the air contained in the tube was replaced by the atmospheric air of the locality, taking the necessary precautions to avoid any mixture of the air of respiration; as soon as the air was collected, the tubes were sealed before the lamp.

I have divided the analyses into three series:—1st, analysis of the atmospheric air of France; 2nd, analysis of the atmospheric air of the Atlantic Ocean and Carribean Sea; 3rd, analysis of the air of New Granada.

The comparison of the results obtained in this investigation with previous ones shows that the constitution of the atmosphere is nearly the same in the New and the Old World. Taking the mean of the analyses, executed in eleven different localities of New Granada, we find that 10,000 vols. of normal atmospheric air contain 4·008 carbonic acid, 2101·425 oxygen, and 7894·557 nitrogen, which are nearly

the same proportions as those which have been found for normal atmospheric air in various parts of Europe. However, on examining carefully all the experiments hitherto made on the constitution of the atmosphere, it is readily seen that the composition of the air is not absolutely constant. Perceptible differences exist, which vary with the meteorological conditions; thus after a long rain the carbonic acid and oxygen are always in smaller proportion than after a long drought; however, these differences are only appreciable when the analysis has been carried out with very great accuracy.

In the New World, where the seasons are more defined than in Europe, these variations are more easily detected. During the fine season the normal air always contains a little more oxygen and a little more carbonic acid than in the season of the rains. Thus, taking the mean of a large number of analyses, I found that 10,000 vols. of normal atmospheric air of Bogota contain—

	With a cloudy sky, and during the rains.	With a bright sky, and during the fine season.
Carbonic acid	3·822	4·573
Oxygen.....	2099·542	2102·195
Nitrogen	7895·636	7893·232

The difference which exists between the atmospheric air of the two seasons is therefore on an average 0·751 for the carbonic acid and 2·653 for the oxygen in 10,000 vols. of air.

Taking the maximum and minimum of the results obtained in the analyses performed during the two seasons, we have—

	During the rainy season.	During the fine season.
Carbonic acid	3·609	5·043
Oxygen.....	2099·032	2103·199
Nitrogen	7897·359	7891·758

The greatest difference amounts consequently to 1·434 for the carbonic acid and to 4·167 for the oxygen. These differences are nearly the same as those which I found between the atmospheric air of Paris and that of Havre, analysed under meteorological conditions corresponding to the two seasons of South America.

It follows that the composition of the air which we respire is the same in Europe and in the New World as far as regards the oxygen and the nitrogen, whether it be taken at the level of the sea or at an elevation of 3000 metres; the only difference is the amount of carbonic acid, which appears, especially on the high mountains, to be somewhat greater than in the valleys and on the sea-shore.

With respect to the analyses of the air collected on the ocean, they have yielded a very interesting result. In the day-time this air constantly contains a little more oxygen and a little more carbonic acid than during the night. This difference becomes more perceptible as we leave the coasts; and it is probably owing to the solar rays, which, heating the surface of the sea during the day, disengage a portion of the gases which the sea-water holds in solution, and which,

as is well known, contains more oxygen and carbonic acid than atmospheric air.

Taking for term of comparison the samples of atmospheric air collected on the Atlantic, on the same day, with the same wind, and at more than 400 leagues distant from land, we find—

	At 3 A.M.	At 3 P.M.
Carbonic acid	3·346	5·420
Oxygen.....	2096·139	2106·099
Nitrogen	7900·515	7888·481

The difference is therefore 2·074 for the carbonic acid and 9·960 for the oxygen in 10,000 vols. of air.

The analyses of the *abnormal* air of New Granada present us with results not less interesting. From time to time, once or twice in the year, the atmosphere of New Granada contains an extraordinary proportion of carbonic acid, which coincides with an appreciable decrease of oxygen, and consequently alters the constitution of the atmosphere in a very marked manner.

The great number of volcanoes which exist in the New World, and the clearing of forests which are effected every year in this country, may cause these alterations. It is, in fact, during these clearances that the constitution of the atmosphere experiences the extraordinary changes which I have just mentioned.

These clearings, which are effected by vast conflagrations, called in the country *las quemas*, produce considerable quantities of carbonic acid, which, mixing with the atmosphere, alter its composition. The amount of carbonic acid which I found in this air rose in some analyses to 49 in 10,000 volumes of air. It is consequently from 10 to 11 times greater than in the air in its normal condition. The diminution of oxygen amounted sometimes to 68·350 in 10,000 vols. of air; instead of 2101·425 oxygen, I found only 2033·075. This decrease is therefore readily detected even by less sensitive methods than the one which I employed.

On the other hand, the air of the plain of Bogota sometimes presents an amount of carbonic acid far greater than the atmosphere of the *tierra caliente*. This difference may be explained either by the existence of volcanoes, which are situated not far from Bogota or by the more or less active influence of the solar light. It will be conceived, in fact, that in the *tierra caliente*, where the temperature is very elevated, the decomposition of the carbonic acid by the green parts of the vegetables must be effected in a far more rapid manner than on the high plain of Bogota, where the temperature is not higher than from 57° to 64° F.

It is perhaps allowable to suppose, on observing this enormous quantity of carbonic acid appear from time to time in the atmosphere of the New World, and considering the large number of volcanoes which exist in the country, that a portion of the carbonic acid of the air is due to them, and that they thus contribute in part to nourish the vast and beautiful vegetation of the tropics.—*Comptes Rendus*, Sept. 29, 1851.

On the Products of Oxidation of Theobromine, and on the Composition of the Rubiaceæ. *By* Prof. Rochleder.

For some time past I have been occupied, in conjunction with Dr. Hlasiwetz, in an examination of the products of oxidation of theobromine. By oxidation with a Grove's battery of nine elements, we have obtained a substance which is represented by the formula $C^{12} H^8 N^2 O^{16}$; and by treatment with peroxide of lead and sulphuric acid, an amorphous substance with the formula $C^{12} H^{13} N^3 O^{12}$. A copious precipitate of ammonio-chloride of platinum is instantly produced in its solution by chloride of platinum. Deducting 1 equiv. of NH^3, HO, there remains $C^{12} H^9 N^2 O^{11} = C^4 H^4, C^8 N^2 H^5 O^{11}$; but the formula $C^8 N^2 H^5 O^{11} = C^8 H^4 N^2 O^{10}$ (alloxane) + HO. The substance contained in the liquid filtered from the ammonio-chloride of platinum crystallizes, but we have not yet prepared it in sufficient quantity for analysis. The formula $C^{12} H^{13} N^3 O^{12}$ might be decomposed into $C^{12} H^8 N^2 O^{10} + NH^3 O + HO$. It would then be a compound of oxide of ammonium (with 1 equiv. of water) with an acid, $C^{12} H^8 N^2 O^{10}$, that is with inosinic acid $+ C^2 H^2$*. Which expression comes nearest to the truth will be shown by the researches in which we are now engaged.

The examination of the different plants belonging to the family of the Rubiaceæ, comprising the following plants,—*Cephaëlis Ipecacuhana, Coffea Arabica, Chiococca racemosa, Cosmibuena* (*China nova*), *China regia, Asperula odorata, Rubia tinctorum, Galium verum* and *Aparine, Richardsonia scabra*,—has, in my opinion, made us acquainted with an interesting law of composition of these members of a natural family.

All these plants contain an acid, which exhibits certain resemblances to tannic acid, and contains 8 equivs. of hydrogen to 14 of carbon, with a variable amount of oxygen, so that its formula is $C^{14} H^8 O^n$. A second series of acids, whose general formula is likewise $C^{14} H^8 O^n$, joins on to the first series; the substances belonging to it have in their properties nothing in common with the series of tannic acids; but both series agree in this, that under certain circumstances 2 equivs. of carbon separate in the form of some compound, so that the formula $C^{14} H^8 O^n$ must be written $C^{12+2} H^8 O^n$. Of the 8 equivs. of hydrogen, 2 equivs. generally separate with the 2 equivs. of carbon, and the formula $C^{14} H^8 O^n$ becomes $\left.\begin{matrix} C^{12} H^6 \\ C^2 H^2 \end{matrix}\right\} O^n$. A third series comprises the substances which contain 12 equivs. of carbon, for instance citric acid, kinovic acid, the red colouring substance of *China nova*, &c. These substances exhibit the remarkable relation that the sum of the equivalents of oxygen and hydrogen in these bodies (the acids considered as hydrates) is

* $C^8 N^2 H^4 O^{10}$ = alloxane.
$C^{10} N^2 H^6 O^{10}$ = inosinic acid.
$C^{12} N^2 H^8 O^{10}$ = the acid of the ammonia salt prepared from theobromine by SO^3 and PbO^2.

This would be a series of alloxane $+ n(C^2 H^2)$, in the same way as alloxantine and amalic acid form a series of alloxantine $+ n(C^2 H^2)$.

either equal to the number 11, or, in the case of citric acid, 2×11, or 22, and in some few cases $=12$. A fourth series, which is not represented in all the plants of the family, is the series of substances with C^{20}, to which quinine, cinchonine, alizarine, &c. belong. Although, judging from the similarity of form, a similarity of composition was highly probable, I do not think it superfluous to have furnished the proof by analysis.

As in the mineral kingdom the garnets, felspars and alums form natural families, one constituent being replaced by an equivalent amount of a very similar one, for instance potash by soda, peroxide of iron by alumina or oxide of chrome, there appears to occur in the families of the vegetable kingdom a substitution of one acid by another very similar in properties and composition.—Liebig's *Annalen*, July 1851.

√ *Experimental Researches on the Æthers and Amides of the fixed Organic Acids. By* P. Demondesir.

Neutral Æthers.—The methods employed to isolate and purify the compound neutral æthers may be reduced to three general processes, distillation, washing with water, and crystallization. The numerous substances belonging to this class hitherto discovered all possess at least one of the properties which ensure the success of the methods; they are all either volatile, sparingly soluble in water, or solid at the ordinary temperature. A large number combine several of these characters.

But if there exist æthers which have none of these properties, it has been impossible to discover them by the usual processes. To this cause I attributed the singular void which occurs in the series of æthers of important organic acids, such as tartaric, paratartaric and malic acids. This hypothesis has been most completely verified. I found that the alcoholic and methylic æthers of these acids are all liquid, are almost entirely destroyed by distillation, and mix with water in every proportion. In this last respect the alcoholic æther of malic acid alone forms an exception; but its solubility in water is still so great, that it is impossible to wash it.

The following is the method by means of which I have succeeded in obtaining these substances. For the ætherification, sulphuric acid or gaseous hydrochloric acid may be employed; but the latter is preferable, as it furnishes under ordinary circumstances more abundant and less coloured products. Moreover the presence of the sulphovinates renders the subsequent purification more difficult.

To isolate the æther formed in this first operation, the acid liquid is neutralized with a carbonate, and shaken repeatedly with sulphuric æther, which removes the compound æther, and furnishes it on distillation. The æther thus obtained still contains water, alcohol, wood-spirit and salts; the volatile substances are first removed by the action of a vacuum or by a gentle heat in the free air, and then the salts by solution in very pure sulphuric æther.

These are the essential points of the general method; but to ob-

tain the largest amount of least coloured and most pure products, it is requisite to modify the details according to the properties of each æther, its affinity for water and the series to which it belongs.

An ordinary preparation gives of pure æther two-thirds at least of the weight of the acid employed, and even an equal weight if the quantities of substances are considerable. These æthers therefore are formed as readily as any others; their purification alone is difficult.

But the use of this method is not limited to the æthers which are very soluble in water, and which cannot be procured by the processes at present in use. In the preparation of these substances, sulphuric æther has sometimes been employed as solvent, and the acids saturated by carbonates; but I am not aware that the two principles have ever been combined to form a general process which appears to me to be applicable to a large number of cases. It is well known what loss is occasioned by washing, especially when operating upon small quantities of material. With respect to the æthers capable of separating from water in the form of an oily layer, sulphuric æther has the property of absorbing the minutest traces which an aqueous solution may contain; we are consequently enabled by this means to obtain the products formed in the ætherification without any perceptible loss. For instance, 250 grms. of citric acid ætherified by sulphuric acid gave 15 grms. of citric æther, purified by washing with water; whilst in a similar operation, with the employment of sulphuric æther, 75 grms. of æther were obtained. The substitution of hydrochloric for the sulphuric acid gave 200 grms., or four-fifths of the weight of the citric acid. For the liquid æthers, which are sparingly soluble in water, and which are not very volatile at the ordinary temperature, sulphuric æther becomes a test for detecting minute quantities and studying the laws of their formation.

Vinic Acids.—In the preparation of the neutral æthers of citric and malic acids, there is always produced some acid æthers. Malic acid gives malovinic and malomethylic acids, the lime-salts of which are soluble in alcohol. Citric acid produces at least one vinic acid having the same character. In the methylic series, the neutral æther is remarkable from its stability and beautiful crystallization. The preparation of the citrobimethylic acid is exceedingly easy; the citromonomethylic acid, which is always simultaneously produced in variable proportions, can be readily separated from the preceding, and also from citric acid, for its lime-salt is very soluble in water and insoluble in alcohol, whilst the citrobimethylate of lime dissolves readily in the latter menstruum.

All these acids are easily produced by the direct action upon alcohol and wood-spirit. According to my experiments, the same method can be advantageously employed for the preparation of the analogous compounds of oxalic acid.

Amides.—The neutral æthers lead immediately to the amides. The action of ammoniacal alcohol upon the tartaric æther of alcohol gives tartramethane or tartramic æther, which, on being carefully

decomposed by alkalies, yields tartramic acid, which is very soluble in water and in alcohol. By continuing the action of ammonia, the tartramethane is converted into tartramide. With the citric æthers the same reagent furnishes, besides several intermediate products which have not yet been perfectly isolated, citramide as the final product in the two series of alcohol- and wood-spirit. Under the same circumstances, malic æther gives malamide, the composition of which does not differ from that of asparagine. Several characters common to these two substances appear to establish their identity. These three amides are very sparingly soluble in cold water, and furnish beautiful crystals. The æthers and amides of tartaric and malic acids act upon polarized light; tartramide especially possesses this property in a remarkable degree.—*Comptes Rendus*, August 25, 1851.

On some Constituents of the Root of Aspidium filix mas. *By* Dr. E. Luck.

From the ætherial extract of the dry root of this fern there is deposited, after distilling off the æther, a yellow, greenish-brown, pulverulent or granular precipitate, which sometimes separates in adherent crusts from thin extracts. Tromsdorff and Kipp obtained from this deposit a substance in yellow crystalline granules, which the first-named chemist called *Filicine*. In 1844 the author examined this substance in Liebig's laboratory, and recently he has again submitted it to further investigation, the results of which he now communicates.

Filicic Acid, $C^{26}H^{15}O^{9}$.—The dry root of *Aspidium filix mas* is exhausted with æther free from alcohol, especially the root collected in autumn, which contains more of the acid than that gathered in spring. The æther is removed by distillation from the clarified extracts until the residue has the consistence of olive-oil; it is then set aside for four or six days, when the impure acid separates. It is first washed with a mixture of equal parts of absolute alcohol and æther, then with a mixture of 2 parts of alcohol and 1 of æther until it has a light lemon colour. It is then dissolved in boiling æther, from which it separates on cooling in the form of a yellowish-white crystalline powder.

It may also be prepared by dissolving the first deposit from the extract in alcohol of 0·912 warmed to between 86° and 104° F., and adding ammonia in small portions until the solution has become turbid; it is then quickly passed through fine linen, filtered through a moistened filter, and poured into a beaker containing hydrochloric acid largely diluted with water. The precipitate, after being washed, is treated with hot alcohol of 0·863 until it no longer becomes coloured;—or the extract of the root is immediately employed. This is diluted with some æther and alcohol in order to render it thinner, 2 vols. of water at 104°, and so much ammonia added that it strongly smells of it, and the whole then well shaken in a stoppered bottle. After the liquid has been set aside some time, two layers form; the

upper one is a dark grass-green fat oil, which will be described further on; the lower one is brown and liquid, and contains the filicic acid. This is separated, quickly filtered through a filter moistened with water, and precipitated with hydrochloric acid. A copious precipitate is formed, which coheres to a plaster-like, yellowish-brown, soft mass, which is kneaded with lukewarm water, and after drying dissolved in boiling absolute alcohol. After filtration and cooling, impure green filicic acid separates from it. It is mixed with cold spirit of 0·863, and this operation repeated.

Filicic acid, when precipitated with acids, forms a whitish-yellow, strongly-adhesive powder, almost like milk of sulphur; from its solution in æther it falls as a crystalline, pale yellowish powder; on quick evaporation, it forms a cauliflower-like vegetation, while on slow evaporation from test-tubes it appears in the form of rhombic plates, the small angles of which are very acute. It is not soluble in water, weak spirit and acetic acid, very sparingly in strong spirit, but dissolves in absolute alcohol on boiling, and again separates for the greater part on cooling. It dissolves in æther, but the solubility is not much increased by heat. It is likewise soluble in fatty oils, oil of turpentine and naphtha, but most readily in sulphuret of carbon. Its odour is slightly balsamic, its taste nauseous; it becomes electrical on being rubbed. At 322° it melts, and then solidifies to an amorphous, greenish-yellow, transparent mass; at a higher temperature it gives off an oily product with the odour of butyric acid. Heated upon platinum foil, it burns with a luminous flame, and leaves a shining cinder. In monohydrated sulphuric acid, it dissolves in the cold with a pale yellow colour; it is precipitated by water, partially unaltered, as a white powder if all rise of temperature has been avoided. When heated, the solution in sulphuric acid acquires an orange colour; fuming sulphuric acid dissolves it with a brown colour.

The ætherial solution of filicic acid turns blue litmus red; solutions of the caustic alkalies heated to 86°–104° readily dissolve it, and froth like soap-water. Heated above 104°, the acid in these salts is decomposed from the absorption of oxygen; with the carbonated alkalies the same salts are formed, when bicarbonated alkali is produced. Filicic acid furnished on analysis—

C.....	63·84	63·57	64·55	64·53	64·78	26	1950	64·20
H	6·45	6·47	6·54	6·30	6·44	15	187	6·17
O	..	..	..	..	..	9	900	29·63

Filicate of Lead, $PbO, C^{26} H^{16} O^{10}$.—The acid is dissolved in carbonate of soda, the bicarbonate produced precipitated by alcohol, and acetate of lead added to the filtered solution diluted with water. The compound falls as a yellowish-white caseous precipitate, which is dried *in vacuo* at the ordinary temperature. It gave on analysis—

Carbon	42·99	42·99	26	= 1950	42·91
Hydrogen	4·19	4·45	16	200	4·40
Oxygen	..	..	10	1000	22·00
Oxide of lead ..	30·84	30·60	1	1394	30·69

Filicate of Soda furnishes, with solutions of salts of the alkaline earths, the earths and heavy metallic oxides, precipitates having the colour generally characteristic of these oxides.

Chlorofilicic Acid, $C^{26}H^{14}ClO^{7}$, HO.—When a current of chlorine is passed over filicic acid contained in a bulb-tube, it is readily dissolved, with evolution of heat, and hydrochloric acid escapes. It is converted into a terebinthaceous mass, which is dissolved in alcohol of 0·863, in order to purify it, and so separate any unaltered filicic acid. On spontaneous evaporation, the solution deposits the chlorofilicic acid in transparent yellowish drops. It is washed in water, and dried at the ordinary temperature.

The acid is insoluble in water, dissolves in alcohol both strong and weak, and in æther, likewise in the fatty oils and in sulphuret of carbon. It has an agreeable fruity smell and a bitter taste; is not crystalline; furnishes, when rubbed, a yellow powder, which cakes together like a resin when warmed, and becomes transparent. The alcoholic solution strongly reddens blue litmus-paper, and solution of acetate of lead produces a precipitate in it. Alkaline liquids dissolve it with a yellow colour. If it be dissolved in a cold solution of carbonate of soda, precipitated by absolute alcohol, and filtered, this solution of chlorofilicate of soda gives a slight opacity with nitrate of silver, which disappears upon the addition of a little nitric acid. Chloride of barium and chloride of calcium give no precipitates; proto- and perchloride of iron cause a dark brown colour, acetate of lead a pale loam-coloured precipitate. When chlorofilicic acid is heated to boiling with carbonated or caustic alkalies, the solution acquires a darker colour, and now furnishes with nitrate of silver a precipitate of chloride of silver. The acid gave on analysis—

Carbon	54·67	26 =	1950	54·47
Hydrogen	5·28	15	187	5·23
Chlorine	12·19	1	442	12·36
Oxygen	27·68	10	1000	27·94

Chlorofilicate of Lead, $C^{26}H^{14}ClO^{7}$, PbO, HO, is precipitated on the addition of acetate of lead to the spirituous solution of the acid, as a pale loam-coloured powder. After the precipitation, the alcohol is diluted with water, as strong alcohol removes acid from the salt.

Trichlorofilicic Acid, $C^{26}H^{12}Cl^{3}O^{9}$, HO, is formed when filicic acid is suspended in water, and chlorine passed into it so long as any is absorbed. The product is collected on a filter and dissolved in alcohol, which is then allowed to evaporate spontaneously.

It forms a yellow powder, insoluble in water, melting in hot water. In alcohol, æther, fatty and essential oils, it is soluble; it has a faint bitter taste and a peculiar odour; the solution has a strong acid reaction. With acetate of lead, it gives a pale loam-coloured precipitate, and behaves in general like chlorofilicic acid. Heated in a test-tube, hydrochloric acid is liberated, and a black shining coal left behind. It furnished on analysis—

Carbon.....	43·80	26 =	1950	43·91
Hydrogen	3·58	13	162·5	3·65
Chlorine	29·81	3	1327·9	29·90
Oxygen	22·81	10	1000	22·54

Trichlorofilicate of Lead, PbO, $C^{26} H^{12} Cl^3 O^7$, HO, is obtained by precipitating a solution of the acid in spirit with acetate of lead. It gave on analysis—

Carbon	33·21	33·40	26 =	1950	33·42
Hydrogen	2·80	2·85	13	162·5	2·78
Chlorine	..	..	3	1327·9	
Oxygen	..	..	10	1000·0	
Oxide of lead..	24·08	..	1	1394·5	23·90

Filimelisic Acid, $C^{24} H^{13} O^8$, is a product of decomposition of filicic acid. It is formed from 4 equivs. of filicic acid by the elimination of butyric acid, when filicic acid is heated with excess of alkali and exclusion of oxygen. Sulphuric acid sets the butyric acid free. Filicic acid is dissolved in dilute solution of caustic ammonia, to which some alcohol has been added, and heated in a vessel filled with an indifferent gas to 176°–212°, and kept some time at this temperature. It is then precipitated with a dilute acid, the precipitate warmed with the liquid, filtered and washed. After drying, it is dissolved in alcohol which has been mixed with some æther, filtered, and evaporated at the ordinary temperature. The filimelisic acid is then left as a loose ochreous powder, which appears under the microscope to consist of minute transparent globules arranged side by side.

It is insoluble in water; very readily soluble in æther, absolute alcohol, and a mixture of the two; less so in spirit; soluble in fat oils and oil of turpentine; easily soluble in sulphuret of carbon. It has a slight odour, and is tasteless. Heated upon platinum, it first melts, and then burns with a bright flame, leaving a shining coal. The spirituous solution has a weak acid reaction; it dissolves in alkaline liquids with an intense yellow colour; a small quantity of this solution imparts a yellow colour to a large amount of water. Concentrated sulphuric acid dissolves it with a brown colour. It gave on analysis—

Carbon	64·74	64·91	65·10	24	=1800	65·02
Hydrogen.....	6·40	6·18	5·90	13	162	5·88
Oxygen.....	29·86	29·11	29·00	8	800	29·10

Filimelisate of Soda is obtained by dissolving the acid in carbonate of soda, and removing the bicarbonate of soda by means of absolute alcohol, which dissolves the soda salt. The solution gives, with chloride of calcium and chloride of barium, pale brown precipitates, with the chlorides of aluminium and magnesium and protochloride of manganese a yellowish, with perchloride of iron a brown, with protochloride of nickel a yellowish-green brown, with protochloride of cobalt a reddish-brown, with bichloride of platinum a dark yellow, with perchloride of copper a brownish-green, and with

perchloride of chromium a green precipitate. No precipitate is produced with perchloride of mercury or nitrate of silver, but with the latter it soon turns dark brown. Acetate of lead gives an ochreous precipitate.

Filimelisate of Lead, PbO, C^{24} H^{13} O^3, HO, is obtained by precipitating a solution of acetate of lead with the soda compound. It gave on analysis—

Carbon.....	41·87	24 =	1800	42·16
Hydrogen	4·21	14	175	4·09
Oxygen	21·60	9	900	21·09
Oxide of lead ..	32·62	1	1394·5	32·66

Filipelosic Acid, C^{24} H^{13} O^9, is a product of decomposition of the filicic acid by oxygen. Filicic acid, dissolved in excess of caustic potash and exposed to the air, absorbs a large quantity of oxygen. Filicic acid is dissolved in very dilute caustic potash by means of heat, and left for about eight days in a shallow evaporating dish, filtered if necessary, and precipitated with dilute sulphuric acid, warmed, the precipitate washed and dried. The liquid contains butyric acid. To separate it from impurities, it may be dissolved in alcohol or a mixture of alcohol and æther, when, on evaporation, the filipelosic acid is left behind as an amorphous mass.

When pulverized, it forms a pale loam-coloured tasteless powder, which has a faint smell of the root. It is insoluble in water, soluble in alcohol with a dark yellow colour, still more so with an addition of æther, or in æther; and soluble in oil of turpentine, fatty oils and sulphuret of carbon. The solution in alcohol and æther has a weak acid reaction, and precipitates acetate of lead. The solution of the soda compound gives a slight precipitate with chloride of barium, with perchloride of iron a brown, with protochloride of iron a chocolate-coloured, with acetate of lead a pale loam-coloured, with bichloride of platinum a yellow precipitate; it behaves consequently precisely like the preceding compound. Nitrate of silver causes no precipitate, but after some time the liquid turns brown; nitrate of copper gives a copious dirty green precipitate. The acid furnished on analysis—

Carbon	62·55	62·98	62·90	24=1800	62·88
Hydrogen	5·75	5·64	5·73	13 162·5	5·67
Oxygen	31·70	31·38	31·37	9 900	31·45

Filipelosate of Lead, PbO, C^{24} H^{13} O^7, HO, is obtained by precipitating the soda compound with acetate of lead. It gave—

Carbon	31·96	..	24 = 1800	41·15
Hydrogen	..	41·15	14 175	4·06
Oxygen	..	4·06	10 1000	22·83
Oxide of lead..	..	22·83	1 1394·5	31·96

It appears that by long-continued action the oxidation of the filicic acid in the alkaline solution may proceed further. The author once obtained a product which furnished on analysis 33·4–34 per cent.

oxide of lead, 40·32 carbon, and 4·07 hydrogen, which numbers correspond to the formula—

$$C^{32}\,H^{13}\,O^{9} + PbO = C^{32}\,H^{12}\,O^{8} + PbO + HO.$$

Chlorofilipelosic Acid, $C^{24}\,H^{12}\,ClO^{9}$.—This acid is produced when chlorine is passed over dry filipelosic acid until no more hydrochloric acid is formed. The product is first washed with water, and then dissolved in a mixture of equal parts of æther and alcohol, filtered, and left to evaporate in the air. It forms an amorphous pale brown mass, has a fruity odour like chlorofilicic acid, a slight bitter taste, and furnishes a brownish-yellow powder; it is soluble in alcohol, but more readily so in æther. It does not dissolve so easily in oil of turpentine, fatty oils and sulphuret of carbon, and is insoluble in water. In the alkalies it dissolves with an intense brownish-yellow colour. On heating the solution in caustic potash, it becomes dark brown, probably with decomposition of the acid and formation of chloride of potassium. On analysis the acid furnished—

Carbon	54·59	24 =	1800	54·68
Hydrogen	4·78	12	150	4·55
Chlorine.....	13·50	..	1	442·6	13·43
Oxygen	27·13	9	900	27·29

Chlorofilipelosate of Soda is obtained by saturating the acid with carbonate of soda, and treatment with absolute alcohol. Alcohol removes the carbonate or bicarbonate of soda, whilst the chlorofilipelosate of soda remains in solution. This furnishes pale brown precipitates with chlorides of barium, calcium, magnesium, manganese, aluminium and acetate of lead, with per- and protochloride of iron a dark brown, with perchloride of iron a greenish-brown, with acetate of uranium a yellowish-brown, and with chloride of platinum a dark yellow precipitate. All these precipitates are flocculent, and shrink considerably together in drying; nitrate of silver is not precipitated; the liquid however soon acquires a dark colour.

Chlorofilipelosate of Lead, $C^{24}\,H^{12}\,Cl\,O^{9}$, PbO, is obtained by precipitating a very dilute solution of the soda compound with acetate of lead. Dried *in vacuo*, it furnished on analysis—

Carbon	38·30	24 =	1800	38·40
Hydrogen	3·22	12	150	3·20
Chlorine	..	1	442·6	
Oxygen	..	9	900	
Oxide of lead	29·31	1	1394·5	29·75

Dichlorofilipelosic Acid, $C^{24}\,H^{11}\,Cl^{2}\,O^{9}$, HO, is produced when chlorine is passed into filipelosic acid suspended in water. When the action is complete, it is dried, dissolved in alcohol, and evaporated at a gentle heat.

It is not crystalline, but separates from an alcoholic or ætherial solution in pale brown drops. When dry, it gives a loam-coloured powder, paler than that of the preceding acid. It melts at a gentle heat, and is decomposed at a higher temperature with disengagement of hydrochloric acid. It is nearly tasteless, insoluble in water,

readily soluble in æther and alcohol, but less so in oil of turpentine, fatty oils and sulphuret of carbon. The spirituous solution strongly reddens blue litmus-paper; it dissolves readily in alkaline liquids with a dark yellow colour. Its reactions are similar to those of the preceding acid. Analysis gave—

Carbon	46·68	24 =	1800	46·93
Hydrogen	4·09	12	150	3·91
Chlorine	23·44	2	885·2	23·08
Oxygen	25·79	10	1000	26·08

Dichlorofilipelosate of Lead, $C^{24}\,H^{11}\,Cl^2\,O^9$, 2PbO, dried *in vacuo*, gave on analysis—

Carbon	27·42	24 =	1800	27·64
Hydrogen	2·15	11	137	2·11
Chlorine	..	2	885·2	
Oxygen	..	9	900	
Oxide of lead	42·95	2	2789	42·83

[To be continued.]

On a new kind of Sugar from Acorns. By M. Dessaignes.

Among the numerous discoveries which organic chemistry owes to that experienced chemist M. Braconnot, one of the most interesting is undoubtedly that of sugar of milk in the fruit of the oak. The small quantity of this sugar upon which he made his experiments did not, it is true, enable him to establish definitively its identity with the sugar which exists in the milk of animals. This question, which is one of considerable interest to vegetable physiology, I have endeavoured to solve. I prepared several grammes of this saccharine substance; and it results from its examination, that it is a body *sui generis* very distinct from milk-sugar, and differing in composition and characters from all the known sugars; it comes nearest to mannite and dulcose. The sugar of the acorn crystallizes in very beautiful prisms, which remain perfectly transparent when obtained by the cooling of a weak alcoholic solution. Heated to 410° F., it does not decrease in weight; at 455° it melts, and then diffuses a vapour which condenses into a slight crystalline sublimate. At this high temperature a very small quantity of the sugar is decomposed, and furnishes a black substance; the remainder, on being dissolved in water, crystallizes without alteration.

Heated with ordinary nitric acid, it furnishes oxalic acid without any mixture of mucic acid. Triturated with strong sulphuric acid, it dissolves without coloration, and forms a conjugate acid, the lime-salt of which does not crystallize. By the action of a mixture of strong sulphuric and nitric acids, it yields a nitrated substance, which detonates, has the appearance of a white resin, is insoluble in water, soluble in hot alcohol; but does not crystallize, and differs in that respect from nitromannite.

The aqueous solution of this sugar may be heated some time with caustic potash without acquiring any colour, and without disengaging

the odour of calomel. It dissolves very little lime, but baryta most readily. It may be boiled for a very long time with a solution of acetate of copper without any reduction of the copper salt. When heated with sulphate of copper and potash, scarcely a particle of protoxide of copper is precipitated after ebullition for a quarter of an hour. It is not precipitated by the subacctate of lead, but the addition of ammonia to the hot liquid causes a copious precipitate, which does not become crystalline in cooling.

The sugar of the acorn mixed with yeast does not undergo alcoholic fermentation; and even when mixed with caseine and water, and left to putrefy for a month in summer, it did not furnish lactic acid, but the entire quantity was reobtained apparently unaltered.

Two combustions with oxide of copper and chlorate of potash gave—

Carbon	43·60	43·88	12 =	43·90
Hydrogen	7·60	7·47	24	7·31
Oxygen	..	..	10	48·79

This is the composition of mannite less the elements of water. To determine the equivalent of this sugar, I dissolved an amount of sugar represented by $C^{12} H^{24} O^{10}$ with 2 equivs. of baryta; on cooling, a large quantity of hydrate of baryta crystallized out. An addition of alcohol caused a further separation of this hydrate, leaving a slightly-coloured gummy solution, which did not crystallize, and which became opake *in vacuo*. Thus dried, this compound contained 29·41 per cent. of baryta, and heated to 302° it lost 5·92 of water. These numbers agree tolerably well with the formula $C^{12} H^{24} O^{10}$, BaO + 2Aq, which requires 29·56 BaO and 7·48 Aq. The difference between the calculated amount of water and the quantity found by experiment, is owing, as I have ascertained, to the absorption of a small quantity of carbonic acid by the substance.

The sugar of the acorn constitutes therefore a distinct and well-defined chemical species, and should consequently receive a name; but I leave to M. Braconnot, its discoverer, the honour of giving it one.—*Comptes Rendus*, Sept. 15, 1851.

On the Nature and Origin of the Acid Principle of the Gastric Juice. By M. Blondlot.

The acidity of the gastric juice has been attributed successively to acetic, phosphoric, muriatic, and more recently lactic acid. M. Blondlot believes that it depends solely upon the presence of biphosphate of lime, notwithstanding the objections which have been made to this view. The reasons for believing that the acid is not one of the four above mentioned are, that the gastric juice does not coagulate albumen; this removes lactic and muriatic acids; and because it does not furnish acetic or any other organic acid on distillation. As regards phosphoric acid, as phosphate of lime exists in the gastric juice, it follows that if phosphoric acid be also present, it must exist in the state of acid phosphate.

A fact as simple as characteristic confirms this view. When the

gastric juice is placed in contact with excess of carbonate of lime, no effervescence ensues, nor does it become perceptibly neutralized. Now as the earthy biphosphates are the only agents among all the acids and acid salts known which react thus, there is a strong presumption for believing that the acidity in question must be attributed to the biphosphate of lime. It is true, it has been objected that if the gastric juice is not neutralized by the carbonate of lime, this depends upon the carbonic acid being held in solution; but this argument is sufficiently refuted, in my opinion, by the fact, that the same negative effects occur at a boiling temperature. It has also been thought, that if the fluid in question does not effervesce with chalk, this depends upon the excessive dilution of its free acid, and the proof of this, it is said, lies in the fact that it does attack it when concentrated; but should we not rather consider that this depends upon the circumstance that a portion of the hydrochloric acid, being disengaged from the chlorides by the biphosphate, under the influence of the heat, is retained in the residue by organic matter, and that it is this acid which attacks the carbonate of lime?

Moreover, I can support my assertion by a direct experiment. After having neutralized some gastric juice with carbonate of soda in slight excess, the solution was filtered, and after concentration was incinerated. The ash was dissolved in water acidulated with a little sulphuric acid at the boiling temperature; the filtered liquid gave with lime-water a perfectly characteristic precipitate of phosphate of lime, which, in the absence of any other phosphate, shows that the acid which held the phosphate of lime in solution was really phosphoric acid in the state of biphosphate.

As regards the origin of the biphosphate of lime contained in the gastric juice, I shall first examine the other inorganic elements in this liquid. When gastric juice is evaporated to dryness, and the residue is carbonized, *muriate of ammonia* is simultaneously volatilized. On washing the charcoal with water, the filtered liquid is perfectly neutral, and not rendered turbid by lime-water, which proves the absence of soluble phosphates. On evaporation, it leaves cubic crystals of *chloride of sodium*, whilst the mother-liquor contains a deliquescent salt soluble in alcohol, *chloride of calcium*. Lastly, the incinerated charcoal furnishes a certain quantity of phosphate of lime, which, as we have seen, existed in it in the state of *biphosphate of lime*. The proportions of the constituents were as follows:—

Water	96·71
Biphosphate of lime	0·60
Chloride of calcium	0·32
Chloride of sodium	0·16
Muriate of ammonia	0·36
Organic matter	1·80
Loss	0·05

What first attracts our attention is the large amount of solid matters in proportion to the water. Lime-salts are especially present in very remarkable quantity. What is their origin? The blood

being alkaline, cannot contain them already formed; but it contains their elements, as the neutral phosphate of lime on the one hand, and chloride of sodium on the other. Supposing the latter to be decomposed in the walls of the stomach into soda, which remains in the blood, and muriatic acid, which reacts upon the neutral phosphate of lime which is in excess, the two salts in question will be produced simultaneously, according to the following formula:—

$$2CaO, PO^5 \text{ (neutral phosphate of lime)} + ClH = CaO, PO^5 \text{ (biphosphate of lime)} + CaCl + HO.$$

As the neutral phosphate yields half its base to the muriatic acid, the quantity of calcium ought to be the same in both the salts produced; now this is, in fact, the case, for 0·60 biphosphate of lime produce, to within an insignificant quantity, as much lime as 0·32 chloride of calcium. This explanation is further supported by the small quantity of chloride of sodium present in the gastric juice, the greater part of this salt having been decomposed to furnish the muriatic acid. Another peculiarity, which establishes this theory, is, that when dilute muriatic acid reacts upon excess of the neutral phosphate of lime, an almost imperceptible trace only of this acid remains in the absolutely free state, which is explained by the well-known laws of affinity; now the gastric juice also contains a trace of free acid, which enables it to tarnish the surface of calcareous spar, but the quantity of which is too small to exert any influence upon the acidity of this liquid.

An electric action in play in the walls of the stomach is the cause to which the decomposition of the chloride of sodium must be attributed. It is at least certain that the above reactions may be produced artificially, by submitting a very simple apparatus, in which neutral phosphate of lime is suspended in a solution of common salt, to the action of a feebly-charged galvanic pile; the soda then goes to the negative pole, whilst at the positive we find a mixture of biphosphate of lime and chloride of calcium, with an infinitesimal trace of free acid.—*Comptes Rendus*, Aug. 4, 1851.

On the Occurrence of Propylamine in Chenopodium vulvaria.

By M. Dessaignes.

A long time ago, MM. Lassaigne and Chevalier pointed out the presence of carbonate of ammonia in *Chenopodium vulvaria*. The analogy between the odour of this plant and that of one of the series of ammoniacal bases discovered by MM. Wurtz, Anderson and Wertheim, viz. propylamine, led me to suspect two years ago that this alkali might occur in that plant. This year I collected a sufficiently large quantity of this plant to submit my supposition to the proof of experience.

I distilled in an alembic about 80 lbs. of the *Chenopodium* in several operations, sometimes with a weak solution of caustic potash, sometimes with a solution of carbonate of soda. The product of the distillation was saturated with hydrochloric acid, evaporated to

dryness, then treated with strong alcohol, which left undissolved a large quantity of chloride of ammonium. The alcoholic solution was precipitated with chloride of platinum, the precipitate washed with alcohol and dissolved in a small quantity of hot water, when it formed on cooling large orange-red crystals of a double salt of platinum and an organic base, which were purified by further crystallization from a small quantity of ammonio-chloride of platinum.

Another method may be employed to obtain a salt of this base free from ammonia. It consists in precipitating the impure hydrochlorate by chloride of gold, and redissolving the precipitate in hot water, from which on cooling a beautiful orange-yellow double salt separates, which is sparingly soluble in cold water, and forms feathery crystals like chloride of ammonium.

The hydrochlorate of this alkali is deliquescent; nevertheless it may be obtained in long prisms by great concentration; it also crystallizes by sublimation. Its aqueous solution mixed with potash disengages an ammoniacal odour, and at the same time an odour of cod-fish or boiled crab. It has the taste of brine which has been employed to salt cod. The double salt of platinum, carefully purified, furnished on analysis numbers which agree perfectly well with the composition of the platino-chloride of propylamine, viz.

Carbon	13·93	6 =	13·57
Hydrogen	3·91	20	3·77
Nitrogen	5·10	2	5·28
Chlorine	40·50	6	40·17
Platinum	37·02	1	37·19

Moreover, the double salt of gold furnished 49·39 per cent. of gold; theory requires 49·62.

Propylamine exists therefore ready formed in a living plant along with ammonia, as proved by its easy liberation on distilling the *Chenopodium vulvaria* with a dilute solution of carbonate of soda. It occurs in this plant along with a large quantity of a proteine compound, which is coagulated by heat.—*Comptes Rendus*, Sept. 29, 1851.

New Method of obtaining Iodine. *By* M. Emil Bechi.

In 1849, the Academy at Florence offered a prize for improvement in the method of obtaining iodine. The proposal referred particularly to procuring the iodine from iodine compounds occurring in the soil at Tuscany. The prize was obtained by M. Bechi. He treated water containing compounds of iodine with a mixture of 1 part sulphuric acid and 2 parts of nitric acid. The water containing the iodine is conducted by a canal to a large vat, in which it is mixed with the acids. The water then contains the iodine separated from the bases. From this it is made to flow into a second vat, which is funnel-shaped below; this is filled with lamp-black which has been heated to redness, like a displacement apparatus with the drug to be exhausted, through which the water containing

the iodineslowly percolates. The lamp-black absorbs the iodine. When this is effected, solution of potash is added to it in a tub, or, what is better, it is mixed with hydrated protoxide of iron. When this action is sufficiently completed, water is allowed to flow to it in a second funnel; this now removes either iodide of potassium with iodate of potash or protiodide of iron from the lamp-black. The funnels containing the charcoal are stopped up below by a sponge. The alkaline solution which flows through is then evaporated to dryness, and the residue distilled with black oxide of manganese and sulphuric acid; or when hydrated protoxide of iron is used, it is treated with sulphate of copper, so as in Serullas' process to precipitate the iodine as iodide of copper, by which means the evaporation is avoided. The iodine is then obtained from this by distillation with black oxide of manganese and sulphuric acid.—*Journ. de Pharm. et de Chim.*, vol. xx. pp. 5–14.

ANALYTICAL CHEMISTRY.

On a new Method for separating Phosphoric Acid from Metallic Oxides. *By* A. Reynoso.

The various processes proposed successively by Berzelius, Otto, Fresenius and H. Rose, for the separation of phosphoric acid from metallic oxides, do not always allow of obtaining a perfect isolation of these substances; a portion of the phosphoric acid is retained by the oxides in the precipitate. It was important to find a method of estimating this acid, especially in the analysis of soils and the ashes of plants, the composition of which is a matter of some importance to agriculture. The following process enables a perfect separation to be effected; it is founded upon an observation of the insolubility of the phosphate of deutoxide of tin in nitric acid, whilst all the other phosphates are soluble in it.

The following is the mode of proceeding:—A weighed quantity of pure tin (tin of commerce may also be used, but the amount of stannic acid which it will produce must have been previously determined) is introduced with the phosphate into a small flask, an excess of nitric acid added, and the whole then boiled. When the whole of the tin has been acted upon, the precipitate is brought upon a filter, washed, and heated to redness over a lamp, weighed, and the quantity of the stannic acid furnished by the tin employed deducted from its weight. The excess in weight gives the quantity of phosphoric acid. It is however necessary to take certain precautions, which if neglected might lead to a loss or an excess. In the first place, it is necessary to avoid any reduction while calcining the precipitate; otherwise the stannic acid would be decomposed, and a loss would result. To avoid this, it will suffice, when incinerating

the filter, to add a few drops of nitric acid, and especially when it is burned over a lamp with a double current to prevent the flame from ascending above the margin of the crucible; otherwise a reduction ensues, which might, it is true, be remedied by the addition of nitric acid, but this may lead to the projection of a portion of the precipitate. In all cases the colour of the precipitate will show whether any reduction has taken place; it should be of a straw colour, not brownish. In the second place, the compound of phosphoric acid with deutoxide of tin very readily absorbs moisture; it is therefore necessary to weigh the precipitate immediately after calcination, and while still warm; otherwise there will be an excess of phosphoric acid.

The accuracy of this process is very easily verified by boiling some phosphate of soda in a flask with an excess of tin and nitric acid diluted with its bulk of water, when the filtered liquid, after saturation with ammonia, gives no precipitate with chloride of calcium. The following are some analyses made by this process:—

Took of pyrophosphate of soda 0·367 grm., of tin 1·000—

	Calculated.	Found.
Phosphoric acid	0·196	0·180
Stannic acid	1·272	1·272

Took of pyrophosphate of soda 0·361 grm., of tin 1·164—

	Calculated.	Found.
Phosphoric acid	0·194	0·182
Stannic acid	1·480	1·480

Took of pyrophosphate of soda 0·200 grm., of tin 1·000—

	Calculated.	Found.
Phosphoric acid	0·107	0·106
Stannic acid	1·272	1·272

Comptes Rendus, October 6, 1851.

PATENT.

Patent granted to John Swindells, *for certain Improvements in obtaining Products from Ores and other matters containing Metals; and in the Preparation and Application of several such Products for the purpose of Bleaching, Printing, Dyeing and Colour-making.*

This invention consists, first, in certain methods of obtaining metals and other products from ores containing copper and silver, or copper only, from ores containing zinc, and from ores containing chromium; and, secondly, in applying part of these products to the purposes of printing, dyeing and producing colour, and also bleaching or discharging colour.

The following is the method of treating ores containing copper

and silver, or copper only:—After the whole or nearly the whole of the sulphur has been extracted by roasting or other suitable means (reducing the ores to oxides), the prepared ore is put into water-tight tanks, and a weak solution of ammonia is pumped thereon until the ore is completely saturated. The strength of the solution is preferred to be about 0·980. The solution is allowed to remain on the ore for a period varying from twelve to twenty-four hours according to circumstances; and when it is drawn off, the ammonia will be found to be saturated with oxide of copper, and if silver be present, with oxide of silver also. The silver and copper may then be separated by any of the usual methods; but it is preferred to precipitate the silver by hydrochloric acid, or salts containing it, and afterwards to separate the copper by hydrosulphuric acid, or salts containing that acid.

To extract zinc from the native sulphuret of that metal, the ore is mixed with about its own weight of common salt, or muriate of potash, or the muriate of any of the earths (common salt however being preferred), and calcined in an oxidizing flame, by a slow protracted heat, until the sulphur is converted into sulphuric acid. Then the products of the operation are separated by dissolving in water the soluble products, which will consist of sulphate of soda, muriate of zinc and muriate of iron; these are separated by first obtaining the sulphate of soda, and then precipitating the oxides of zinc and iron by lime, or any other alkaline earth or substance; and the oxide of zinc is afterwards smelted in the ordinary manner.

Ores containing chromium are treated in the following way:—The ore is first pulverized, and mixed with its own weight of common salt, or muriate of potash, or hydrate of lime. Then, if it is desired to obtain a product containing soda as the alkali, the mixture of ore and common salt is subjected, in a reverberatory furnace, to a full red heat, or even to a white heat; at the same time a jet of steam at a very elevated temperature is applied; and the mixture is stirred every ten or fifteen minutes until the required effect is produced, which will be ascertained by taking a small quantity of the mixture from the furnace and testing it. When the process is finished, the product will be chromate of soda, the hydrochloric acid having carried away the whole or nearly the whole of the iron in the shape of sesquichloride of iron; and the product withdrawn from the furnace is treated as usual in the manufacture of chromic or bichromic salts. The mixtures of ore with muriate of potash and of ore with hydrate of lime are also treated in the manner just described. From the mixture of ore and common salt, pure bichromate of soda is manufactured, and by the addition of hydrochloric acid, chlorochromate of soda is produced. From the lime mixture, chromate of lime is manufactured, or, by the addition of soda or potash, a compound salt of soda or potash and lime.—Sealed Nov. 14, 1850.

THE CHEMICAL GAZETTE.

No. CCXVIII.—November 15, 1851.

SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Bark of Cinchona nova. *By* H. Hlasiwetz.

The investigation of this bark (called also *Cinchona Surinamensis*) was undertaken for the purpose of completing, with reference to the Rubiaceæ, the chemical investigation of whole families of plants, as suggested by Prof. Rochleder. The principal constituents are a tannic acid, the so-called cinchona-red, the kinovic acid discovered by Pelletier and Caventou, and according to Gruner a peculiar alkaloid. These bodies have all been partially investigated except the tannic acid, which I believe must be considered as a peculiar kind; it only remained therefore to ascertain what possible connexion there might exist between them, and to supply some other deficiencies in the knowledge of some of them. The following results which I have obtained may perhaps contribute in some degree to the solution of this problem:—

Chinova-tannic Acid.

The aqueous decoction of this bark is dark red-brown, rather turbid, and contains the greater part of the tannic acid, partly in solution, partly mechanically suspended, much cinchona-red, some kinic acid, kinovic acid, gum and mineral salts.

Acetate of lead throws down from this solution a chocolate-brown precipitate, which contains all the sulphuric and phosphoric acid present in the bark, almost the whole of the cinchona-red, and a small quantity of tannic acid. This precipitate is voluminous, and at the same time mucilaginous and difficult to filter.

It is of no further use for the preparation of the tannic acid. The liquid remaining after its separation is tolerably dark-coloured, and is most advantageously divided into three equal parts, of which one is completely precipitated by basic acetate of lead, and then mixed with the remaining two-thirds. By this means a light brown precipitate is obtained, which contains that part of the kinovic acid extracted from the bark by water, the last traces of cinchona-red and some tannic acid. It is not worth while extracting this portion of tannic acid, and the precipitate is therefore put on one side. After its separation, the liquid is considerably lighter-coloured; and on a fresh addition of basic acetate of lead, a brownish-yellow precipitate of chinova-tannate of lead is formed.

This lead salt was well washed, and decomposed under water by

sulphuretted hydrogen. The filtered liquid was then gently heated in order to drive off the excess of sulphuretted hydrogen, the last traces of which were removed by acetate of lead. The neutral acetate of lead precipitates the acid only in very small quantity, and therefore the brown precipitate consists chiefly of sulphuret of lead. After this had been removed, a large quantity of strong alcohol was added to the clear liquid containing an excess of acetate of lead, by which it was rendered turbid, and by gently heating, deposited a light flocculent precipitate, which was the pure lead compound of the chinova-tannic acid.

After decomposing this salt under water, removing the sulphuret of lead and excess of sulphuretted hydrogen, a solution of pure tannic acid remained, which had a dark yellow colour, and an astringent, rather bitter taste. It was evaporated to dryness by the heat of a water-bath in a retort, through which a continuous stream of carbonic acid was passed. When it had acquired the consistence of an extract, the bottom of the retort was cracked off, and the evaporation completed in a steam apparatus. Thus prepared, the acid appeared as a transparent, amber-yellow, brittle mass, easily reducible to a light powder, forming a perfectly clear solution with water and alcohol, but insoluble in æther. Its aqueous solution is, even when extremely dilute, coloured dark green by perchloride of iron; ammonia produces a brown colour, which becomes gradually more intense. It may be boiled with dilute inorganic acids without any perceptible change; it has no action on a solution of gelatine; it reduces the salts of silver and gold, and does not precipitate tartrate of antimony and potash. In contact with the solutions of the alkalies and alkaline earths, it is readily oxidized by the atmosphere; the metallic oxides, not precipitated by sulphuretted hydrogen from acid solutions, afford no salts suitable for analysis. Oxide of lead is almost the only base which enters into permanent combinations with this, as with most other unerystalline tannic acids, although at the same time in very variable proportions. I was therefore compelled to deduce a formula for this acid from the analyses of several lead salts and of the dried acid, and in other respects to be guided by the nature of its decomposition and its connexion with the cinchona-red.

The analysis of the acid and its lead compounds, dried at 212° F., lead to the formula $C^{14}\,H^{8}\,O^{7}$, HO.

The tannic acid from coffee has the same composition, but the two acids differ essentially in their reaction with ammonia, which in this case gives a brown colour, and with the acid from coffee a green, as well as in the manner in which their respective formulas must be viewed, to which I shall afterwards refer again.

The per-centage composition of the chinova-tannic acid is as follows:—

Carbon.....	51·62	52·02	28 = 168		52·01
Hydrogen	5·89	5·82	19	19	5·88
Oxygen	42·49	42·16	17	136	42·11

$=2(C^{14}\,H^{8}\,O^{7}, HO) + Aq.$

A lead salt, prepared by precipitating a solution of the pure acid with basic acetate of lead, carefully washed and dried at 212° F., gave on analysis in 100 parts—

Carbon	29·99	..	140 =	840	30·12
Hydrogen	3·08	..	89	89	3·18
Oxygen	22·67	..	79	632	22·69
Oxide of lead....	44·26	44·29	11	1227·1	44·01

After deducting the oxide of lead, the composition of the acid would be—

Carbon	53·80	14 =	53·50
Hydrogen	5·52	9	5·67
Oxygen	40·64	8	40·83

leading to the formula $C^{14} H^9 O^7$, HO, and the salt itself $= 10(C^{14} H^9 O^7) + 11PbO + 9HO$.

A second lead compound was obtained by a different mode of preparation. After the partial precipitation for the purpose of separating the kinovic acid, the light precipitate obtained by further precipitation by basic acetate of lead was decomposed under strong alcohol, and the solution of the acid thus obtained precipitated by an alcoholic solution of acetate of lead. This compound was of a very light colour. It was washed with alcohol, and dried at 212° F. It furnished—

Carbon.....	26·30	26·51	28 =	168	26·26
Hydrogen	2·64	2·70	17	17	2·65
Oxygen	19·00	18·90	15	120	18·87
Oxide of lead	52·06	51·89	3	334·68	52·31

answering to the formula $= 2(C^{14} H^9 O^7, PbO) + PbO$, HO.

The pure acid, after deduction of the oxide of lead, is—

Carbon	54·86	28 =	55·08
Hydrogen	5·50	17	5·57
Oxygen	39·64	15	39·35

A third lead salt must be mentioned here, which was prepared in a manner quite different from the former.

An alcoholic infusion of the bark was precipitated by acetate of lead. The yellow liquid filtered from the red-brown precipitate was freed from excess of acetate of lead by sulphuretted hydrogen ; and after separating the sulphuret of lead, the greater part of the alcohol was distilled off in a retort. The only slightly alcoholic residue was then poured into a large quantity of water, by which the kinovic acid was precipitated somewhat impure. The filtered liquid still contained the tannic acid and the alkaloid, in case there was one present. The addition of basic acetate of lead and a few drops of ammonia produced a beautiful yellow precipitate, which, decomposed under water by sulphuretted hydrogen, afforded a red-yellow liquid, which still contained traces of kinovic acid. This was therefore removed, as before, by a partial precipitation by basic acetate of lead, and only the second precipitate thus produced was collected. This compound, decomposed under strong alcohol by sulphuretted

hydrogen, gave a dark yellow solution of the acid, which, after expelling the excess of gas, gave all the above-mentioned reactions, and was not precipitated by acetate of lead. Basic acetate of lead gave a yellow lead salt of the following composition, in 100 parts—

Carbon.....	29·20	..	56	= 336	29·22
Hydrogen	2·89	..	32	32	2·78
Oxygen	19·49	..	28	224	19·58
Oxide of lead	48·42	48·59	5	557·8	48·42

When from the formula of this salt, $=4(C^{14}H^{8}O^{7})+5PbO$, the oxide of lead is deducted, there remains for the acid in combination—

Carbon	56·7	14 =	56·8
Hydrogen	5·6	8	5·6
Oxygen	37·7	7	37·6

The chinova-tannic acid cannot be combined with oxide of copper without decomposition. On the addition of the acetate or of the hydrated oxide of copper to a solution of it, a dark greenish-brown colour is immediately produced. Strong alcohol indeed throws down a dirty green compound in flocks, but the acid contained in it is oxidized, and the copper reduced to the state of suboxide. The formula of the acid combined with the suboxide has thus become $=C^{14}H^{7}O^{8}$.

The presence of suboxide of copper may be easily detected. Such a salt dissolved in water, which may be done by boiling, gives on cooling a yellowish-red precipitate of suboxide of copper with caustic potash. The analysis of two copper salts, of which the first was prepared with a solution of the pure acid, the second with the liquid which the second lead salt had afforded, gives data justifying this view. Both salts were dried at 212° F., and gave in 100 parts—

First Copper Salt.

Carbon	44·73	56 =	336	45·07
Hydrogen.....	4·77	34	34	4·56
Oxygen.....	41·83	39	312	41·86
Copper	8·67	2	63·44	8·51

$=4(C^{14}H^{7}O^{8}, HO)+(Cu^{2}O, HO)+Aq.$

After deduction of the protoxide of copper, there remains in 100 parts—

Carbon	49·56	42 =	49·41
Hydrogen	5·28	26	5·09
Oxygen	45·16	29	45·50

$=3(C^{14}H^{7}O^{8}), 5HO.$

Second Copper Salt.

For this the formula $2(C^{14}H^{7}O^{8}, HO)+Cu^{2}O, HO$ was deduced; and after deduction of the protoxide of copper, there remained for the acid, in 100 parts—

Carbon	47·52	42	= 47·72
Hydrogen	5·60	28	5·30
Oxygen	46·88	31	46·98

$=3(C^{14}\,H^{7}\,O^{8}), 7HO.$

This simple and demonstrable oxidation in the copper compounds of the acid $C^{14}\,H^{8}\,O^{7}$ to $C^{14}\,H^{7}\,O^{8}$, which is also the formula of the viridic acid produced from the tannic acid of coffee, seems to favour the correctness of the formula, on which account I have described them in detail.

From a comparison of the results of the analyses of the pure acid and its lead compounds, I believe that I may venture to assign to it the formula $C^{14}\,H^{8}\,O^{7}$.

I have before remarked, that, in accordance with this view, it is isomeric with the tannic acid of coffee, and it now remains to show what evidence there is against their identity.

Chinova-red.

The substance to which I give this name, to distinguish it from the red colouring matter of other cinchona barks, occurs ready-formed in large quantity in this bark. The first lead precipitates produced, as well in aqueous as in alcoholic infusions of the bark by neutral acetate of lead, contain it almost exclusively. When these precipitates are decomposed by sulphuretted hydrogen under water, the tannic acid, &c. which they contain is dissolved, and the chinova-red remains mixed with the sulphuret of lead, from which it may be separated by boiling in alcohol, and pouring the concentrated solution into a large quantity of water, when it separates readily as a brown-red flocculent precipitate. In consequence of its solubility in alkalies and caustic ammonia, it may also be prepared by digesting the bark in dilute ammonia, and precipitating by hydrochloric acid.

When the product of either process is washed upon a filter until the water running from it no longer gives any green colour with perchloride of iron, it may be considered entirely free from all adhering tannic acid. But it still contains a certain quantity of kinovic acid, which always remains mixed with it in those modes of preparation. This is separated by boiling with milk of lime made of pure caustic lime, repeated until the filtered liquid is no longer rendered turbid on the addition of an acid, by the precipitation of kinovic acid, for which purpose four or five treatments are required. The chinova-red enters into combinations with the solutions of the hydrates of alkaline earths, which are not soluble in water, while the kinovic acid is known to be easily soluble. This lime compound is now decomposed by hydrochloric acid, the solution of chloride of calcium filtered off, and the chinova-red washed with distilled water until the droppings no longer give any reaction with nitrate of silver. It is then advantageous to dissolve it again in dilute ammonia, precipitate as before, and wash the precipitate thoroughly with hot water. On treating the still moist mass with alcohol, it dissolves with the exception of a very unimportant residue, which is separated by fil-

tration. The dark red liquid thus obtained, poured into a large quantity of water, gradually deposits very delicate flocks of perfectly pure chinova-red.

When dried, it forms almost black brilliant masses, which have the appearance of a resin. The powder is dark red; it is almost insoluble in water, but easily soluble in alcohol, æther and alkalies. It is not altered by dilute acids; perchloride of iron gives no perceptible colouring with the alcoholic solution. An alcoholic solution of acetate of lead precipitates it entirely. When heated, it burns, evolving an empyreumatic odour, without leaving any ash. Dried at 212° F., the analysis gives the following results in 100 parts:—

Carbon	61·10	61·32	12 =	72	61·01
Hydrogen	5·05	5·26	6	6	5·08
Oxygen	33·85	33·42	5	40	33·91

The formula of the chinova-red stands therefore in a simple relation to that of the chinova-tannic acid, from which it differs by a deficiency of $C^2 H^2 O^2$:—

$$C^{14} H^8 O^7 - C^{12} H^6 O^5 = C^2 H^2 O^2.$$

It is extremely probable that this $C^2 H^2 O^2$ is contained in the chinova-tannic acid as a hydrate of carbon. For if a solution of this acid is boiled for some time with a little dilute sulphuric acid, the still undecomposed acid and the sulphuric acid precipitated by basic acetate of lead, and the excess of this removed by sulphuric acid and filtration, a slightly-yellowish liquid remains, which affords a perfect sugar reaction with a solution of hydrated oxide of copper in caustic potash, red oxide of copper being precipitated.

The pure chinova-tannic acid has not this property. I have also repeatedly remarked, that concentrated solutions of the acid, after long exposure to the air, deposit a red powder, which dissolves in ammonia and alcohol, and cannot well be anything else than chinova-red.

This will perhaps also account in part for the fermentation of an aqueous infusion of the bark, which readily takes place if it is exposed to a constant temperature of 59° F.

I am consequently of opinion that the chinova-tannic acid must be considered as a conjugate compound of $C^{12} H^6 O^5 + C^2 H^2 O^2$, and that the latter group of atoms is to be considered as a hydrate of carbon, since, according to previous investigations, the same group of atoms represents the aldehyde of formic acid in the isomeric tannic acid of coffee.

G. Liebich has described the products of the action of potash upon the tannic acid of coffee in vol. vii. p. 462 of this Journal, and shown that it also yields a compound, $C^{12} H^6 O^5$, which by further oxidation passes finally into $C^{12} H^4 O^7$.

The chinova-red suffers an analogous oxidation in its lead compounds, which I have repeatedly prepared and examined. I will merely give one example. A lead salt, of a red-brown colour, prepared from alcoholic solutions of acetate of lead and chinova-red, well washed and dried at 212° F., had the following composition:—

Carbon	59·40	24 =	144	59·75
Hydrogen.....	3·84	9	9	3·73
Oxygen.....	36·76	11	88	36·76

$=2(C^{12}H^4O^5)+HO.$

If in $C^{12}H^6O^5$, 1 equiv. HO is replaced by 2 equivs. O, there results $C^{12}H^5O^6$, or what is the same, $C^{12}H^4O^5$, HO.

Gum.

The liquid from which the pure chinova-tannate of lead has been precipitated contains gum, or an isomeric hydrate of carbon. If the excess of acetate of lead is removed by sulphuretted hydrogen, there remains after filtration a colourless solution, which yields on evaporation a brownish extract. I could not detect sugar in this; it was not until the liquid had been boiled for a long time with dilute sulphuric acid that I obtained a very distinct reaction with a solution of oxide of copper in potash. Moreover, if such a solution, containing free acetic acid, is exposed for a long time to the atmosphere, the hydrate of carbon is converted into, first, grape-sugar, and afterwards apoglucinic acid, at least such I consider to be the composition of two lead salts which I obtained from such liquids, and whose other characters corresponded with those which are assigned to the various compounds of apoglucinic acid with oxide of lead. Both were almost white. Dried at 212° F., they gave on analysis—

First Lead Salt.

					Deducting the oxide of lead.			
C	18·19	36 =	216	18·4	C	54·6	18 =	54·27
H	1·99	21	21	1·7	H	5·9	11	5·53
O	13·09	17	152	13·2	O	39·5	10	40·20
PbO	66·73	7	780·92	66·7				

$=2(C^{18}H^9O^8), 7PbO+3Aq.$ $=(C^{18}H^9O^8, HO)+Aq.$

Second Lead Salt.

					Deducting the oxide of lead.			
C	15·33	54 =	324	15·55	C	51·20	54 =	51·18
H	1·69	37	37	1·77	H	5·65	37	5·84
O	12·88	34	272	13·07	O	43·15	34	42·98
PbO	70·10	13	1450·28	69·61				

$=3(C^{18}H^9O^8)+13PbO+10Aq.$ $=3(C^{18}H^9O^8,HO)+7Aq.$

[To be continued.]

On the Regeneration of Mannite and Quercite from Nitromannite and Nitroquercite. *By* M. Dessaignes.

The nitrogenous substances produced by the combination of nitric acid with organic substances with the elimination of water have never yet been, so far as I am aware, except in the nitric æthers, metamorphosed so as to reproduce the organic substance, whence they are derived, by substituting hydrogen for the nitric residue N^2O^4, which they contain. I have succeeded in effecting

this substitution in two bodies of this class, viz. nitromannite and nitroquercite. [I have, with the approbation of M. Braconnot, given the name of quercite to the sugar discovered in the acorn. See p. 413.]

Highly-concentrated hydrosulphate of ammonia, saturated with sulphuretted hydrogen, and containing even some bisulphuret of ammonium, is the reagent I employ to effect this reduction, which is very precise, especially with the nitroquercite. I dissolve the perfectly washed nitrogenous substance in alcohol with the assistance of heat, and add rapidly a large excess of hydrosulphate of ammonia. An enormous quantity of ammonia is disengaged, and much sulphur is deposited in the liquid, which is quickly evaporated on the water-bath. The dry residue is redissolved in hot water, and filtered. With nitroquercite the filtered liquid is nearly colourless, and on evaporation deposits large crystals, which are easily purified, and present all the characters of quercite. Dried *in vacuo* and analysed, they furnished, C 43·69 and H 7·71; theory requires C 43·90 and H 7·31. The nitromannite upon which I operated had been crystallized from alcohol and well washed; it could not therefore contain any mannite uncombined with nitric acid. The crude product of the reaction is colourless, especially if the hydrosulphate employed is not too concentrated; and it contains in this case a considerable amount of an ammonia salt of an organic acid. The evaporated liquid yields a crystalline mass, which is strongly pressed in paper, and which, on being redissolved and decolorized by animal charcoal, deposits on spontaneous evaporation prisms of a sweet taste, which present the characters of pure mannite. In fact, when dried *in vacuo* and analysed, they gave C 39·69 and H 8·03; theory requires C 39·55 and H 7·68.—*Comptes Rendus*, Oct. 27, 1851.

On the Gases which are enclosed in the internal Cavities of Plants. *By* Ad. Knop *and* Dr. W. Knop.

Since the commencement of the spring of the present year, we have been engaged in the study of the gases which are enclosed in the internal cavities of plants. The results which we have at present obtained are not sufficiently numerous to allow of our making general deductions from them. Our reason for publishing the following preliminary observations is, that MM. Cloet and Gratiolet*, in the publication of their results, have already anticipated us in some of those which we also obtained. The experiments of these two French observers were commenced some years ago; hence their results are of greater extent than ours. We also, for the same reason, lay no claim to the individual observations being contemporaneous; although their observations were made in a different point of view from our own, they agree; but we are convinced that the principles hitherto laid down must be greatly limited in their general application.

In our experiments, the larger plants among those growing on the

* Ann. de Chim. et de Phys., xxxii. p. 41.

banks of rivers and in bogs were principally selected, and the gas was collected from the lowest joints,—those situated nearest to the roots, then the middle leafy portions, and lastly the uppermost, or those situated nearest to the flowers. Among the land-plants, we selected those, the stems of which are divided by nodes; these were cut through below a node, and the cut portion immediately put into a vessel of water, so as to collect the gas on the spot from the upper nodes in graduated tubes. The gas was afterwards measured, and the oxygen absorbed by phosphorus, its complete absorption being controlled by the eudiometer. Hitherto we have only determined the relative proportions of the nitrogen and oxygen, since, in regard to carbonic acid, our method of collecting the gases, so as to prevent its addition to or removal from them by the water of displacement, introduced difficulties which could only be overcome at the expense of more time than was at our disposal. Determinations of the carbonic acid will be made hereafter. In the experiments we have as yet made, the quantity of it present was extremely small.

It is our intention to continue these investigations for several years. We shall now merely detail those results in which the greatest differences were observed, without at present drawing any general conclusions from them.

The stem of *Potamogeton crispus* was cut across, in May, and exposed to the light of the sun, in the same water as that in which it was growing; a gas was evolved from the cut surface, in which a glowing shaving immediately took fire. The gas, when shaken with solution of potash and treated with phosphorus, was found to consist of—

Oxygen	92
Nitrogen	8

When the stem was cut off close above the root, gas was also evolved from the section. It was distinctly seen with a lens, that the gas issued from the parts which botanists call the intercellular spaces. The question of the part played by the oxygen in the vicinity of the roots was also mooted by MM. Cloez and Gratiolet. We endeavoured to ascertain this in June, July and August, from the hollow horizontal rhizomata of the grasses, as the roots of *Potamogeton* were not adapted for this purpose. Large aquatic grasses were placed in a glass tube six feet in length, which was closed below by the surface of water, and a copious current of carbonic acid was conducted into it from below. After some time, the glass tube was closed at the top with a bladder, and the plants in their natural position were left for one, two or three hours in the air surcharged with the carbonic acid, exposed with a clear sky to the full sunshine. The plant was then quickly drawn down into the water, and the gas squeezed from the culm and the hollow rhizomes. As yet no sufficiently important difference has been found between the composition of the gases from parts of the plants at different heights and those from the same plants in the natural state, to allow of our forming a conclusion as to the relation between the variation in the composition of the gases in the root, even when the gas in which the leaves exist alters; but these experiments must be repeated. Small bubbles of gas

are also observed on the leaves of *Potamogeton crispus*. But it is difficult to decide whether these become attached from without, or proceed from within. When the sun's light is kept off the cut stems of the plants by a cloud, the bubbles of gas are evolved more slowly.

Although, in general, our observations confirm those of MM. Cloez and Gratiolet, in one important point we obtained a totally different result from these observers. Thus, in a piece cut from the middle of a stem of *Potamogeton perfoliatus*, they found that gas was only evolved from the cut surface of the stem nearest the root, even when the piece was placed in different positions. We found, on the other hand, when a piece had been cut from the middle of a plant of *Potamogeton crispus*, to which a lateral branch bearing several leaves was attached, provided that both ends of the branch were equally distant from the point of attachment, that the gas exactly obeyed the laws of hydrostatics. It issued from the upper section when the section next the root-end occupied a lower position than the upper, and *vice versâ*.

MM. Cloez and Gratiolet from their experiments draw the conclusion, that the gases traverse the stem in a definite current, taking a direction from the leaves towards the roots, and suppose that this current is constant.

In our observations upon *Potamogeton crispus*, the following appears to us to be the fact:—The leaves evolve in the course of a day, when exposed to the light of the sun, more gas than they are able to contain when the stem is wounded, or even completely cut through. The direction which the current of gas takes is not determined by any peculiar action of the cells of the plant; it rather obeys the ordinary laws of physics, and the gas escapes where it finds least resistance. The internal cavities of intercellular spaces of the stem become filled by the copious development which takes place in the cells of the leaves, or by the tension of the gases contained in the interior of the plant to which it gives rise, and the cells of the leaves are the only parts in which the existence of a definite direction can be assumed to exist; in the intercellular spaces, the phænomena concerning the gas are the same as in ordinary tubes. Regard must be paid, in the interpretation of these various phænomena, to the structure of the stem and to the determination of the direction in which there is least resistance in the air-passages of the stem. Hence we do not consider this evolution of gas as the consequence of a normal current from the leaves towards the root, but that the current itself is only observed under abnormal circumstances; the intercellular passages down to the root are filled with gas of greater tension than that of the atmosphere; it therefore escapes when one wound or several are made, according to purely physical laws. In the month of July, the same spots in those plants which in May evolved gas copiously, ceased to give off any more; they were still perfectly healthy, but covered with a thin muddy coating.

The cut stems of *Myriophyllum spicatum* gave off in July a gas, which contained only 33 per cent. of oxygen, although during the day in which the gas was collected and several following days there was full sunshine. The expansion of the gas was distinctly

observed in this plant; when the stem was placed horizontally, and the rate at which the bubbles of gas ascended was observed, it was always found that when the plant was placed so nearly perpendicular that the section giving off the gas was uppermost, it was accelerated; whilst retardation occurred when the glass tube was so placed that the section was downwards, so that the gas had to displace a higher column of water before it escaped.

We are of opinion, that in those naturally healthy uninjured aquatic plants which when wounded evolve gas spontaneously, the gas is confined under a certain amount of tension, which very probably maintains the equilibrium of the developing force in the leaves at a certain period, so that the amount of gas which is evolved from the injured plant is not consumed in the uninjured plant. The amount of the gas evolved by aquatic plants is not dependent upon the sun's light only. The gas mentioned above as obtained from *Myriophyllum spicatum*, and which is of the same composition as the air dissolved in water, was collected in full sunshine, and at a time when, for several days previously, uninterrupted full sunshine had existed. Hence the influence of the age of the plant and the season of the year must be further examined. The nitrogen gas, which is evolved in the course of 10 hours by *Myriophyllum*, occupies altogether more space than the entire plant itself. Some other plants, which were not immersed in water, but only partially covered by it, did not spontaneously evolve gas during the summer from the hollow rhizomes or torn portions. We shall subjoin some further results of the examination of the gases from the interior of plants; these will be extended in a subsequent communication:—

Experiments at Noon.

Plant.	Part.	Month.	Temperature.	Sky.	Proportion. O. : N.
Trapa natans.	Petiole.	June.	60° F. in the water.	Full sunshine.	20 : 80
Alisma plantago.	Peduncle.	July.	53° F. in the water.	Full sunshine.	19 : 81
Alisma plantago.	Peduncle beneath the panicle.	August.	60° F. in the water.	Sky cloudy, atmosphere misty.	20 : 80
	Internodes between the uppermost and lowest flowers.				19 : 81
	Petiole.				20 : 80

Experiments in the Evening.

Phellandrium aquaticum.	Root.	July.	53° F.	Troubled.	4 : 96
Poa aquatica.	Lowest three submersed internodes.	July.	60° F. in the water.	Changeable.	14 : 86
Sagittaria sagittifolia.	Peduncle with expanded flowers.	July.	57° F. in the water.	Changeable.	18 : 82
	Petiole.				18 : 82

Pharm. Central-Blatt., Aug. 27, 1851.

On the Occurrence of Vanadium, and on the Preparation of pure Vanadic Acid. By J. Fritzsche.

Schubin proved, in 1839, and on several subsequent occasions, that the products of the Perm smelting-works contained vanadium. In a cupreous sandstone, in which, with the help of a lens, vanadiate of copper was recognized as a constituent, he found on analysis 0·53 per cent. of vanadic acid; in another sandstone not a trace of vanadium could be detected. The pig-iron containing copper, obtained in the smelting of the Perm ores, which Schubin described as being so hard that both instruments made of cast steel, as well as of the pig-iron itself, were immediately rendered useless in some experiments made to bore a cylinder from it, he found to have the following composition:—

Carbon	3·03
Vanadium	1·99
Silica	2·51
Copper	12·64
Iron	75·97
Aluminum	0·89
Magnesium	0·78
Calcium	0·95
	98·76

The black copper obtained at the same time with the cupreous pig-iron he found to contain,—carbon, 0·94; vanadium, 1·21; copper, 90·52; iron, 6·17. In two slags of different composition he found 1·57 and 1·30 per cent. of vanadic acid; and he likewise found, in various other products, some vanadium, but considerably less in quantity.

Fritzsche operated upon a far larger amount of the Perm pig-iron in order to obtain the vanadic acid. For this purpose the pig-iron was digested with dilute sulphuric acid, when the fragments gradually became covered with a granular coating, on which the sulphuric acid had no further action, and which, especially when it had acquired a certain thickness, either separated spontaneously from the pig-iron or could be easily detached from it. These crusts, which had not the appearance of a skeleton left untouched by the acid, but appeared rather to have been formed by the reduction of substances which had been previously in solution, proved on examination to contain a very large amount of vanadium, whilst the solution contained so little vanadium that it was not worth while attempting to separate it. Moreover, the metallic copper which had been mechanically mixed with the pig-iron, and of which a considerable amount was left after the complete solution of the iron, was not further examined.

The granular crusts, which from their slight cohesion generally fell to a coarse powder on drying, were treated with nitre to extract the vanadium. They were mixed with an equal weight of crystals of nitre, and heated in an iron spoon; as soon as the nitre began to

melt, violent action ensued; the mass puffed up considerably, owing to the disengagement of red vapours, and the heat evolved was so great that the whole mass was in an intense glow, which rendered any further heating to complete the reaction scarcely necessary. The semifused mass obtained in this manner was when cold exhausted with water, and the vanadium precipitated from the filtered solution by chloride of ammonium as vanadiate of ammonia.

The vanadiate of ammonia thus obtained is not pure; it still contained some silica, which accompanies the vanadic acid prepared from it, and can only be completely removed from it, as stated by Berzelius, by hydrofluoric acid.

Fritzsche proposes another method of purifying the vanadic acid. A salt of vanadic acid with either of the fixed alkalies was first prepared, the hot tolerably-concentrated aqueous solution of which was gradually mixed with nitric acid, when a brownish-red, bulky, flocculent precipitate separated, and the liquid, after being sufficiently heated with an excess of the acid, now contained but little vanadic acid in solution, which imparted to it a pale yellow colour, and at least partially separated on evaporation in the form of the above reddish-brown amorphous substance. The precipitate was collected on a filter, well washed, and dried at the ordinary temperature; it now formed a light brownish-red powder, which was heated with twenty times its weight of monohydrated sulphuric acid. At first a perfectly clear solution, of a deep yellow colour, was formed; but on the continued application of heat, a crystalline product began soon to separate, which was a compound of vanadic acid with sulphuric acid, the quantity of which increased to such an extent that very soon the whole mass formed a paste. It was now cooled, the crystals separated from the liquid by decantation, then collected in a funnel, with the narrow part drawn out into a fine point, after which the mother-liquor having drained off, they were washed with the hydrate of sulphuric acid until this passed off colourless, when they were placed upon a porous tile under a bell-glass, where they were left over sulphuric acid until the sulphuric acid adhering to the crystals had been absorbed. The tolerably dry crystalline powder was heated in a platinum dish, first to expel the sulphuric acid, and then to melt the vanadic acid, which on cooling solidified into a beautifully crystalline mass, perfectly free from every impurity. In this manner more than 70 grammes of pure vanadic acid were prepared.

In this preparation of the vanadic acid, however, the entire amount contained in the reddish-brown substance is far from being obtained as sulphate; a very considerable portion remains in the sulphuric acid mother-liquor. In one experiment, made with weighed quantities, 65·76 per cent. of fused vanadic acid was obtained; there had consequently remained dissolved in the sulphuric acid no less than 34·24 per cent. This solution furnished, after it had been mixed with some water and evaporated to expel the sulphuric acid, a pulverulent crystalline product, which under the microscope appeared to consist of two different crystalline compounds. The one

belonged to the prismatic system, and had the appearance of the above-described compound; whilst the other formed tabular crystals of a much darker yellow colour, and among which were many rectangular parallelograms with the corners truncated. From an analysis made of this mixture, it was found that the tabular compound contained 3 atoms of sulphuric acid to 1 of vanadic acid.

The greater portion of the vanadic acid held in solution in the sulphuric mother-liquor can also be separated in the form of other compounds, when the acid is diluted with water mixed with alcohol, and then evaporated. If only so much alcohol has been added as is necessary to reduce the vanadic acid to the state of oxide, light blue, microscopic, four-sided prisms are deposited, probably the sulphate of vanadium; on the other hand, if more alcohol has been added, on concentrating the acid to its highest degree, a considerable foaming occurs, together with the formation of ætherial products, and the separation of another crystalline substance.

The above-mentioned reddish-brown pulverulent substance appears to be a hydrate of vanadic acid; if it be dissolved in sulphuric acid at 212°, and then the excess of acid quickly dissipated, the previously-mentioned pale orange compound of sulphuric acid with vanadic acid separates as a crystalline powder; the amount of vanadic acid in it, however, varies from 46 to 50 per cent.—*Bulletin de St. Pétersbourg*, ix. p. 196.

On a new Method of preparing the Tungstate of the Oxide of Tungsten and Soda. By H. Wright.

This interesting compound was discovered by Prof. Wöhler in 1824; and, as far as I am aware, has never been prepared except according to the method originally described, by heating the bi-tungstate of soda in dry hydrogen. I have attempted to prepare it by acting upon the same salt with other reducing agents, and with perfect success; it may be readily produced by the action of phosphorus, zinc and tin upon the heated tungstate; of these, tin is the best adapted for the easy preparation of this beautiful substance. For this purpose, take the crystallized tungstate of soda rendered anhydrous, or the salt which is obtained when tungstic acid and carbonate of soda are fused together in the proportion of 2 equivs. to 1 equiv., and so much tungstic acid added to the fused mass as it will dissolve. This may be done in a porcelain crucible over a large spirit-lamp. Tin is now added to the melting mass in little pieces. The formation of the cubes on the surface of the melting tin is immediately perceptible; they are seen to grow, and soon to fill the entire mass. This crystallization is the more wonderful, since the cubes themselves are not at all fusible at this temperature, and the largest, so it appeared to me, were not formed in immediate contact with the tin. For the success of the operation, and in order to obtain large and beautiful crystals, it is requisite to employ a temperature which just suffices to fuse the salt, and that the process last for a very short time. I obtained far less satisfactory results in some experiments which I made at a higher temperature with a charcoal

fire, and continued for several hours; the excess of tin appearing to alter the cubes formed. In this way I sometimes obtained it not with a yellow but with a purple metallic lustre. Once however the operation succeeded perfectly well by mixing the powdered bi-tungstate with about one-tenth of its weight of tin filings, and heating the mixture in a glass tube placed in a crucible and surrounded with sand, until the glass became soft. On cooling, I obtained a mass filled with golden cubes. To isolate the crystals, they are alternately digested with concentrated solution of potash and hydrochloric acid; finally, washed with water, and dried. If there was an excess of fused tin, it is generally covered with cubic crystals. In this manner I have obtained them very perfect, and with a golden-yellow metallic lustre. The surfaces of the larger ones are not quite smooth, but have terrace-like depressions, as in the case of bismuth.

Their specific gravity I found to be 6·617. They are perfect conductors of the electric current. If brought into contact with zinc under dilute sulphuric acid, hydrogen is liberated at their surface. In contact with zinc in a solution of copper, they become coated with copper. I have analysed the crystals by decomposing them with sulphur, and subsequently oxidizing the mass with aqua regia:—

1·848 grm. gave 1·729 tungstic acid, or 93·55 per cent.
1·065 grm. gave 0·997 tungstic acid, or 93·61 per cent.

According to the formula $WO^2\,WO^3 + NaO\,WO^3$, 93·8 per cent. ought to have been obtained.—Liebig's *Annalen*, August 1851.

On some Constituents of the Root of Aspidium filix mas. *By* Dr. E. Luck.

[Continued from p. 413.]

Action of Sulphuric Acid on Filicic Acid.—Monohydrated sulphuric acid dissolves filicic acid; water separates from the solution a compound insoluble in water, on which account the solution becomes turbid when exposed to the air in a watch-glass. When the solution is poured into water, a yellowish-white precipitate falls, which is in part unaltered filicic acid. When the action is continued longer, and on the application of heat, the filicic acid is decomposed, butyric, acetic and sulphurous acids being formed, whilst the precipitates by water constantly become darker. They all contain sulphur or sulphuric acid, do not precipitate chloride of barium, and are soluble in alcohol. The amount of sulphur calculated as sulphuric acid varied; the author found 7·7, 4·01, 4·21, 11·62, 6·31 per cent. sulphuric acid.

Fuming sulphuric acid immediately dissolves filicic acid at the ordinary temperature; when poured into water, a yellowish-brown precipitate falls, which, after the sulphuric acid water has been poured off, dissolves in water. The wash-water contains butyric acid. When the action of the sulphuric acid has continued from two to three hours, the precipitate by water dissolves entirely after washing out the acid. The product is a conjugate acid, viz.

Sulphofilimelisic Acid, $C^{24}H^{13}O^{8}, SO^{3}$.—It is prepared in the following manner:—Filicic acid is triturated in a mortar with 6 to 8 parts of fuming sulphuric acid; after from two to four hours the brown liquid is poured into a cold dilute aqueous solution of sulphate of soda, avoiding a rise of temperature, on which account the precipitation is made at intervals. The brown precipitate is collected on a filter, and washed with a cold solution of sulphate of soda until what passes through has no longer an acid reaction. It is pressed between paper, and dried at a gentle heat. The mass, which is covered with an efflorescence of sulphate of soda, is now treated with hot absolute alcohol or æther, which leaves the sulphate of soda behind and dissolves the acid. After filtration and evaporation at a gentle heat, the acid is left as a brownish-yellow, transparent, fissured mass.

It does not crystallize; is sparingly soluble in cold, readily in hot water, alcohol and æther; it has a bitter taste, and furnishes a golden-yellow powder; it turns blue litmus-paper slightly red, and dissolves in alkaline liquids with a dark yellow colour. It dissolves in barytic and lime-water; and if carbonic acid be passed through the barytic solution, the excess of baryta is precipitated as carbonate, whilst the neutral compound remains in solution. On evaporation, it is obtained as an amorphous mass, which furnishes a bright minium-red powder. The aqueous solution of this barytic compound is not precipitated by nitrate of silver; acetate of lead gives a pale yellowish-red, and if some ammonia has been previously added to the barytic compound, a copious brick-red precipitate. The protochloride of manganese gives a copious pale brownish-red, perchloride of iron a brown, protochloride of iron a chocolate, bichloride of platinum a yellow, nitrate of copper an olive-brown, acetate of uranium a yellowish-brown, and chloride of aluminium a light reddish-brown precipitate. This acid is formed from the filicic acid by the separation of butyric acid from 4 equivs. filicic acid, and the conjunction of the remainder with sulphuric acid. Sulphofilimelisic acid furnished on analysis—

Carbon	55·32	24 =	1800	55·17
Hydrogen	5·29	13	162·5	4·98
Oxygen	23·90	8	800	24·49
Sulphuric acid	15·49	1	501·16	15·36

Sulphofilimelisate of Baryta, $BaO, C^{24}H^{13}O^{8}, SO^{3}$.—An aqueous solution of the acid is gradually saturated with barytic water, evaporated to dryness, and this operation repeated until the residue dissolves to a clear solution. The salt forms a minium-red mass, the solution of which in water is reddish-yellow; it has a bitter sweet taste, and gave on analysis—

Carbon	42·35	24 =	1800	42·66
Hydrogen	3·90	13	162·5	3·85
Oxygen	..	8	800	
Sulphuric acid	..	1	501·16	
Baryta	23·07	1	956·9	22·68

Sulphofilimelisate of Lead, PbO, C^{24} H^{13} O^8, SO^3, is obtained by mixing the barytic compound with a solution of acetate of lead, in the form of a yellowish-red precipitate. It gave on analysis—

Carbon	38·34	24 =	1800	38·65
Hydrogen	3·57	13	162·5	3·48
Oxygen	..	8	800	
Sulphuric acid	..	1	501·16	
Oxide of lead	29·32	1	1394·5	29·94

Basic Sulphofilimelisate of Lead, 4PbO, C^{24} H^{13} O^8, SO^3, forms a brick-red precipitate, which is obtained when the solution of the acid is mixed with some ammonia previous to the addition of the acetate of lead. This precipitate furnished on analysis—

Carbon	20·10	24 =	20·36
Hydrogen	1·87	13	1·83
Oxygen	..	8	
Sulphuric acid	..	1	
Oxide of lead	63·49	4	63·10

The Fat Oil of the Root of the Fern.—The ætherial extract of the root of the fern contains, as already stated, a fat oil besides the filicic acid. If it be diluted first with æther and alcohol, and then with twice the amount of hot water, and some ammonia added, the liquid separates into two layers, the lower one of which contains the filicic or filimelisic acid, and the upper one a fat oil. This latter is separated, and, after being well shaken with water, dried over chloride of calcium.

It has a dark grass-green colour; by transmitted light appears puce-colour; did not become congealed by exposure to the cold of a severe winter; did not lose its green colour from frequent exposure during the year to the air; smells like the root, and tastes at first mild, but subsequently acrid and bitter. It is not easily saponified by potash; the soda soap does not become solid.

Filicicolic Acid, C^{42} H^{40} O^4, HO.—If the oil saponified by potash is decomposed with sulphuric acid, a liquid green oily acid is procured. To obtain it pure, it was dissolved in an excess of ammonia, precipitated with chloride of barium, the washed barytic salt dissolved in hot alcohol, and in this manner a perfectly white baryta salt prepared, whilst the green colour remained in solution. From this salt, acids separated the pale yellow hydrated filicicolic acid. It had a strong acid reaction, no smell, and but a slight taste. It gave on analysis—

Carbon	75·06	42 =	3150	75·67
Hydrogen	12·58	41	512·5	12·31
Oxygen	12·36	5	500	12·02

Filicicolate of Baryta, BaO, C^{42} H^{40} O^4, prepared as above stated, furnished—

Carbon	62·51	42 =	3150	62·91
Hydrogen	9·96	40	500	9·98
Oxygen	8·35	4	400	8·00
Baryta	19·18	1	957	19·11

On destructive distillation, the impure green filicicolic acid behaves like ordinary oleic acid; the distillate contained sebacic acid and some volatile acids, the baryta salts of which appeared to be a mixture of caprate and caproate of baryta.

Filosmylic Acid, $C^3 H^2 O^3$, HO.—When the aqueous liquid from which the filicicolic acid has been separated by sulphuric acid is distilled, a volatile acid passes over. The distillate is saturated with barytic water, the excess of baryta removed by carbonic acid, the concentrated liquid purified with animal charcoal, and set aside to crystallize; this salt contains a volatile acid, which possesses the offensive odour of the root. One analysis of the baryta salt furnished—

Carbon	14·85	3 =	225	14·62
Hydrogen	2·08	2	25	1·65
Oxygen	19·87	3	300	19·93
Baryta	63·20	1	956·9	63·50

[To be continued.]

On a new Method of preparing Nitrogen and Chlorine. *By* E. J. Maumené.

Numerous processes are known for the preparation of nitrogen, but excepting that by the decomposition of air by metals they are all wanting in simplicity. The following will perhaps appear preferable, *although it furnishes chlorine at the same time.* This process consists in acting with nitrate of ammonia upon the hydrochlorate of the same base at a moderate temperature. According to theory,

$$2(NO^5 H^3 NHO) + H^3 NHCl = 5N + Cl + 12HO,$$

with which experiment agrees. As soon as the mixture attains the melting-point of the nitrate, a brisk reaction ensues, and it furnishes the above results. As soon as the reaction commences, the mixture is removed from the fire, and the decomposition proceeds nearly to the end entirely of itself.

This mode of preparation might prove dangerous for two reasons,—1st, because it furnishes with great rapidity products which are all gaseous, so that with any considerable quantity of substance there would always be a chance of explosion; and, 2nd, because the mixture of the two salts forms a paste, puffs up considerably, and is very liable to produce a complete obstruction in the neck of the retort. These difficulties are easily avoided; it suffices to employ but a small quantity of the mixture at a time, and to add to it about 4 times the quantity of sand; it then becomes the most easy experiment. Take 75 grms. of dry nitrate of ammonia, 25 dry muriate of ammonia, and 400 grms. of sand; these proportions yield 26 litres of dry nitrogen and 5 litres of chlorine.

I think it superfluous to observe, that the heat is sufficiently high to leave no fear as to the production of the chloride of nitrogen. The gases never had the faintest smell of it. When the above pro-

portions for the mixture are observed, and when the salts are pure, nothing but water, nitrogen and chlorine are obtained.

This new mode of production of chlorine without manganese, and with substances which every day become cheaper, will perhaps prove interesting.—*Comptes Rendus*, Oct. 13, 1851.

On a new Organic Matter forming the Substance of certain Tubercles of the Serous Membrane of the Alimentary Canal, the Heart and the Liver. By MM. CHEVALLIER *and* LASSAIGNE.

In examining the body of a young woman which had been interred for two months, small warty and whitish rounded bodies, of the size of a poppy-seed, were found upon the serous membrane covering the stomach, the small intestines, the liver, the pericardium, and in the substance of the liver itself.

The matter appears to be peculiar in its nature; it bears some resemblance to cystine, which was discovered by Wollaston in 1812 in human vesical calculi, and which has since been found in a few other instances only. The authors call these new bodies provisionally *cystinoid tubercles*, and the peculiar substance they contain *xanthocystine*. When heated in a platinum spoon, it does not melt; before frothing up, it becomes yellow, then black, and evolves brownish-yellow fumes; the odour resembles that of burnt horn. The vapour which is given off from them when heated in a glass tube has an alkaline reaction.

The substance is insoluble in water and alcohol; mineral acids and ammonia however dissolve it. The nitric and muriatic acid solutions deposit crystals on evaporation; those from the former are slightly yellow. When the ammoniacal solution is evaporated, small white grains are obtained. The forms in this residue bear great resemblance to those obtained from cystine in the same manner. The quantity of the substance obtained was too small to allow of the satisfactory determination of its nature. It appears to be intermediate between cystine and xanthine.—*Journ. de Chim. Méd.*, vol. vii. pp. 208–212.

On the Presence of Iodine in the Atmosphere and the Absorption of Iodine in Respiration. By A. CHATAIN.

From the wide distribution of iodine in spring- and river-waters, the author concluded that it would also be found in the atmosphere. A large aspirator, by means of which the air was drawn through several Liebig's apparatus, in which the iodine was collected, was used for the experiments; from which it resulted that 4000 litres of Paris air contain one five-thousandth of a milligramme of iodine. Bearing in mind that a man inspires daily 8 cubic metres, or 8000 litres of air, it will be found that he daily introduces one two-hundred-and-fiftieth of a milligramme of iodine through the mucous membrane of the lungs into the blood. In some localities the amount of iodine

received through the air is greater than that which is imbibed with the potable water.

The author likewise examined the air expired by him in twenty-four hours; it had lost four-fifths of its iodine.

In the rain-water of Paris the author found one-fifth, one-fourth, one-third and one-half milligramme in 10 litres of water, an enormous amount when calculated for the total amount of rain. Considerable fluctuations occur in the amount of iodine at one and the same place, and it has hitherto been found impossible to divine the cause. In the course of the months of February, March and April, the amount varied from 1 to 6; other fluctuations were met with between these, and were observed at different localities in France.

The results of the examination of the rain-water on the sea-coast are highly remarkable; for instance, at Bayonne, Biaritz, Havre, and Dunkirk, the rain was found to contain less iodine than in the interior of the country. The rain contained about $\frac{1}{30}$th milligramme of iodine in 10 litres of water. Rain collected on the same day at Biaritz furnished $\frac{1}{250}$th, at Bayonne $\frac{1}{390}$th iodine to the litre, whilst that at Paris, Clermont, Verdun and Provins, gave $\frac{1}{1000}$th.

It results from a series of long-continued observations, that the rain which falls last after a continued fall contains less iodine. The author found less iodine in the snow of the 10th of March than in rain which fell soon afterwards; he found more in hail which fell on the 2nd of May at Versailles than in the rain which followed. He also found iodine in dew.—*Journ. de Pharm. et de Chim.*, xix. p. 421.

Detection of Mercury in the Body of a Person dying of Mercurial Cachexy. *By* M. Gorup-Besanez.

The subject was a woman, who was for twenty-five years laboriously engaged in silvering looking-glasses, but who, from the convulsive tremors that were induced, had been obliged to desist from her occupation for a year prior to death.

The chemical results obtained by following the processes of Fresenius and Babo were as follows:—The lungs and heart gave no trace of mercury; a very small quantity was detected in the liver and none in the bile. A doubtful precipitate was thrown down upon the gold plate by the brain, while the spinal column presented no traces. That any remains at all should be found after a year is remarkable, and is confirmatory of other facts, proving how long certain metals, *e. g.* antimony, may be retained in the œconomy. That the liver was the only organ in which it could then be detected, confirms the doctrine that metallic poisons are usually found longest in that organ.—Buchner's *Repert.*, vii. 178; *Med. Chir. Rev.*

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Bark of Cinchona nova. *By* H. Hlasiwetz.

[Concluded from page 427.]

Kinic Acid.

Stenhouse first examined cinchona bark for this acid, but did not succeed in obtaining it*.

His experiments were however made on such a small quantity of bark (1 oz.), that it might easily be overlooked.

In my experiments for the detection of this acid, I employed 1 lb. of broken bark. The decoction was treated while hot with milk of lime, the whole filtered, and sulphuric acid added until it was slightly acid; the kinovic acid and some sulphate of lime were thus separated. The liquid was filtered and evaporated to about half. It was then poured into a capacious flask, sulphuric acid and oxide of manganese added, and the flask connected with a condensing apparatus. The mixture frothed up on heating, and it was only after some considerable time that a quiescent ebullition commenced. A yellow fluid then passed over, which had an acrid smell, and gave the most distinct reactions of quinone.

The kinic acid must exist as such in the bark, for neither the chinova-tannic acid nor the chinova-red yields a trace of quinone when treated with oxide of manganese and sulphuric acid.

Kinovic Acid.

The method adopted for the preparation of this acid is either that given in the description of the third chinova-tannate of lead or that proposed by Winckler, which is equally advantageous, of boiling the bark (the better if it has been once infused in water, by which the greater part of the contaminating chinova-red is removed) with milk of lime, and adding an excess of hydrochloric acid to the filtrate. In both cases an impure, more or less yellow-coloured product is obtained, which is most readily separated from foreign admixtures by again boiling in milk of lime, decolorizing the filtrate by animal charcoal, precipitating with hydrochloric acid, and re-

* Liebig's Annalen, vol. liv. p. 100.

peating this treatment until it appears in snow-white flocks. The method of purification by means either of repeated solution in ammonia and precipitation with an acid, or of solution in alcohol and precipitation by water, is much more tedious, since in both cases the most important cause of impurity, the chinova-red, is again taken up and precipitated.

A small quantity of the kinovic acid is dissolved, as I had occasion to remark before, by the water in which the bark is boiled. If such a boiling decoction is mixed with milk of lime, filtered, and precipitated by hydrochloric acid, a portion of the acid is obtained impure, which does not become perfectly white until after repeated purifications. The pure kinovic acid is, when thrown on a filter, a voluminous gelatinous mass, which is extremely difficult to wash. Its purity cannot be relied upon till after several days' washing, and then, as it cannot be pressed, it must be taken from the filter, and dried in a dish by a gentle heat. It contracts very much in drying, and finally appears as a light brittle mass resembling gum, which becomes remarkably electrical when rubbed, and affords a brilliant white powder. The kinovic acid is however a constituent not only of this so-called false cinchona bark (*Cinchona nova*), but is also contained in nearly as large quantity in the best *Cinchona fusca**, so that it may be partly detected in the aqueous decoction, and the greater part of it obtained by the methods previously described.

Schnedermann† has furnished the most recent investigation of this interesting substance. From the analyses of the pure acid and some of its salts he assigned to it the formula $C^{38}H^{29}O^{7}+HO$. The numbers from which this formula is deduced refer to an acid which was dried in a water-bath. Schnedermann states that at this temperature all the water was driven off; according to him it then contains no more water separable by heat, and he ascribes the loss of weight which the acid still suffers when dried *in vacuo* to hygroscopic moisture. But, according to my own experiments, the acid does not become free from water until it has been either several months in a vacuum, or exposed for a considerable time to a temperature of at least 320° F. It even remains unaltered for some considerable time at 356°–374° F.; but if, after such drying, all the water is driven off, the per-centage composition corresponds to the formula $C^{12}H^{9}O^{3}$. The following analyses of the acid, dried at different temperatures, will testify to the correctness of this formula:—

a. Dried at 212° F., in 100 parts.			*b.* Dried at 284° F.		
C.... 66·05	60	66·30	C.... 66·57	120	66·85
H.... 8·93	47	8·65	H .. 8·88	93	8·63
O.... 25·02	17	25·05	O.... 24·55	33	24·52
$=5(C^{12}H^{9}O^{3})+2Aq.$			$=10(C^{12}H^{9}O^{3})+3Aq.$		

* According to the researches of R. Schwartz.

† Liebig's Annalen, xlv. p. 277.

	c. Dried at 320° F.*			*d.* Dried at 356° F.			
C	68·90	68·80	12	68·57	C .... 68·33	12	68·57
H	8·85	8·87	9	8·57	H .... 9·03	9	8·57
O	22·25	22·33	3	22·86	O .... 22·64	3	22·86

c and *d* = $C^{12}H^{9}O^{3}$.

Schnedermann's numbers finally lead to the formula $5(C^{12}H^{9}O^{3}) + Aq$:—

C	67·06	67·07	67·04	67·34	60 =	67·41
H	9·13	8·96	8·95	8·91	46	8·61
O	23·81	23·97	24·01	23·75	16	23·98

Consequently Schnedermann's acid contains 1 equiv. water to 5 equivs. of the acid, and approaches nearest to the acid *a*, which contains 2 equivs. of water to 5 equivs. of acid.

As the salts of this acid are, according to Schnedermann's researches, not very definite compounds, the correctness of the formula $C^{12}H^{9}O^{3}$ may perhaps be better inferred from the products of decomposition described below than from the salts. This formula is the same which Professor Rochleder and myself have assigned for the chlococcic acid obtained from the cainca acid, and the identity of the two may in fact be readily proved by a few experiments. Their external characters are exactly the same. Both are gelatinous when moist; their manner of drying and appearance when dry are the same; both are soluble in the same proportion in alcohol, alkalies and solutions of alkaline earths; both have an intense bitter taste, and are dissolved by concentrated sulphuric acid with a red colour. When heated, they melt, evolving at the same time an odour like frankincense, and burning with flame. The correspondence between their analyses is stated in another place†. It is necessary to state that the analysis there given, corresponding to the formula $C^{12}H^{9}O^{3}$, refers to an acid which had been dried by remaining for three months under the exhausted receiver of an air-pump.

Lastly, both acids undergo the same kind of decomposition. When submitted to dry distillation, a limpid, cloudy, acid liquid, of an empyreumatic odour, distils over at the commencement by a moderate heat. On raising the temperature, a thick, clear, amber-yellow liquid appears, which solidifies in the neck of the retort, may be easily detached from the sides, and resembles a light resin somewhat closely.

The success of this experiment is rendered rather difficult by the violent frothing and almost unavoidable running-over of the melted acid. This unfavourable circumstance is entirely prevented by previously mixing the acid with about an equal bulk of silicic acid.

The first liquid is readily miscible with water, reduces nitrate of silver and nitrate of mercury with great ease, yields with caustic potash a brown resin and an odour like cinnamon, and dissolves hydrated oxide of lead. In short, it presents all the characters of the

* These two analyses were of the acid prepared from *Cinchona fusca*.

† Liebig's Annalen, lxxvi. p. 341.

aldehyde of acetic acid. The formula of aldehyde trebled gives the formula of kinovic acid, $3(C^4 H^3 O) = C^{12} H^9 O^3$.

The resin produced by the decomposition at a very high temperature, purified by solution in alcohol, evaporation to dryness and fusion in a water-bath, gives on analysis—

Carbon	85·44	34 =	85·71
Hydrogen	10·93	26	10·92
Oxygen	3·63	1	3·37

It may be assumed that in the formation of this resin 4 equivs. of the acid is decomposed in the following manner :—

$$4(C^{12} H^{9} O^3) = C^{48} H^{36} O^{12} = C^{34} H^{26} O + 5(CO^2) + 9(CH) + HO,$$

according to which carbonic acid, carburetted hydrogen and water will be formed as collateral products.

The acid is decomposed in an entirely different manner when distilled with lime. In this case water passes over first, then a yellow oleaginous liquid, and finally the same brown resin, which is however soluble in the oily liquid, on account of which the whole appears viscid and fatty. The odour of these products is empyreumatic, and resembles metacetone. In order to separate them, they were distilled with water, when the resin remained in the retort, and the yellow liquid passed over, and then presented a positive odour of metacetone and the other characters of it. It was shaken with a little caustic potash, again distilled, and dried over chloride of calcium. The quantity left after this purification was only sufficient for one analysis, the result of which is only so far available and explanatory of the nature of the liquid, that it testified to the relation of the carbon to the hydrogen being as 6 : 5, so that there can be no doubt that metacetone is actually formed.

An attempt to form an amide, or some similar body, by the action of dry ammonia upon the melted acid, had not the desired result. The acid was placed in a bulbed tube, the extremity of which bent down and dipped into water. On applying a gentle heat until the acid was fused, thick vapours were formed, which condensed slightly upon the tube in small milky drops, and finally solidified apparently in a crystalline form ; but the quantity was so small that it was quite impossible to collect it. By continued heating, the above-mentioned resinous product was again formed, as when the acid was heated alone.

At ordinary temperatures oxidizing substances scarcely attack the acid at all, but on the application of heat a tolerably energetic action commences. I have examined in detail the products of the action of boiling nitric acid. By this means the acid is partially dissolved with a yellow colour ; part remains in the form of a white granular powder. If the action is continued until the evolution of nitrous vapours ceases, and water then added, a beautiful white flocculent substance is separated. When the whole has been placed on a filter, and freed from the excess of nitric acid by washing, then pressed between paper, and treated with hot alcohol as long as anything is taken up, a yellow alcoholic liquor is obtained, which on

evaporation leaves a light yellow resin, and a snow-white granular powder, which is insoluble in water and alcohol. Both substances contain nitrogen or nitrous acid, and burn with flame when heated, evolving the same odour of frankincense peculiar to the pure acid. There is no oxalic acid in the nitric acid liquor, and neither fatty, acetic nor formic acids are formed. The following formulæ may be calculated from the results of the analysis of both substances:—

Resin $= C^{20} H^{13} O^{8}$.
White body $= C^{24} H^{15} O^{11}$.

If the sum of both $= C^{44} H^{28} O^{19}$ is deducted from 4 equivs. of kinovic acid $= C^{48} H^{36} O^{12}$, there remains $C^{4} H^{8}$, and an increase of 7 equivs. oxygen. It is possible that $C^{4} O^{3}$ is separated from the compound in the form of carbonic acid and water. The per-centage numbers which lead to these formulæ are—

Resin.

Carbon	60·94	20 =	60·91
Hydrogen	6·67	13	6·59
Oxygen	32·39	8	32·50

White Substance.

Carbon	58·35	24 =	58·30
Hydrogen	6·10	15	6·07
Oxygen	35·55	11	35·63

The kinovic acid exists in the bark, most probably in combination with lime. I have not yet been able to determine whether it is formed from a constituent of the bark (perhaps the kinic acid), as the chiococcic acid from the caincic acid.

I was not able to obtain from my undoubtedly genuine bark the alkaloid which the *Cinchona nova* is said to contain. I boiled 5 lbs. of broken bark in water acidulated with sulphuric acid, precipitated the decoction with basic acetate of lead, separated the precipitate, and freed the remaining liquor from excess of lead salt by sulphuretted hydrogen. The filtrate from the sulphuret of lead gave, on evaporation, a very dark liquid, which was warmed for some time with caustic lime. Upon cooling, the pasty mass was boiled with alcohol repeatedly. The coloured alcoholic solution contained lime which was separated by sulphuric acid, and I attempted to obtain the sulphuric acid salt of the base by evaporating the alcohol; but only a very small quantity of a brown uncrystallizable syrup was left, which had scarcely any bitter taste, and whose solution was not in the slightest degree precipitated by ammonia.

On treating another 5 lbs. in the more customary way of preparing the cinchona alkaloids, by precipitating the decoction of the bark in dilute sulphuric acid by milk of lime, and boiling the lime precipitate with alcohol, I was not more fortunate. I was therefore compelled to conclude either that the bark contained no alkaloid, or that at least it was not present in my bark. The former

appears to be the more probable, from the absence of any medical properties in the bark.

In conclusion, I will briefly state the results of the above investigation:—

1. The chinova bark contains a tannic acid, which is isomeric with the tannic acid of coffee $= C^{14} H^8 O^7$. The difference from it depends upon the way in which its constitution is viewed, viz.

$$C^{12} H^6 O^5 + C^2 H^2 O^2 = C^{14} H^8 O^7.$$

2. The substance to which the colour of the *Cinchona nova* is principally owing, the chinova-red, has the formula $C^{12} H^6 O^5$, and in all probability is formed in the plant from the tannic acid.

3. One of the principal constituents of the bark, upon which also its bitter taste depends, the kinovic acid, is identical with the chiococcic acid obtainable from caincic acid, and is composed of $C^{12} H^9 O^3$. This acid moreover yields, under different circumstances, aldehyde, metacetone, and a resin of the composition $C^{34} H^{26} O$. It is oxidized by nitric acid in such a way that 4 equivs. of carbon and 8 equivs. of hydrogen are eliminated, and 7 equivs. of oxygen taken up. By this change a white amorphous body and a light yellow resin are formed.

4. The bark contains kinic acid.

5. It is highly probable that it contains no vegetable base.

A subsequent article, by Professor Rochleder, upon the chemical relations of the family Rubiaceæ, will show what place the constituents of this bark occupy in the series of compounds belonging to this family.—Liebig's *Annalen*, vol. lxxix. p. 129.

On the Presence of Sugar in the Urine. *By* M. Reynoso.

The author believes that the presence of sugar in the urine, after wounding the brain just above the origin of the eighth pair of nerves, is to be attributed to a different cause to that assigned by M. Bernard. He reminds us that the portion wounded, as M. Flourens has shown, is the true seat of the respiratory function; and that, as a consequence of the injury caused by the wound, paralysation, either complete or partial, of the respiration takes place. Hence the normal sugar is no longer capable of being burnt off, and passes into the urine. To prove this, means must be found to impede the respiration by producing asphyxia; and experiment has shown that in anæsthesia sugar may be produced in the urine.

If this view be correct, the quantity of sugar present should be greater in proportion to the activity of the respiration of the animal subjected to ætherization. Now less sugar is found in the urine of herbivorous than in that of carnivorous animals. In the case of two men subjected to ætherization, the one yielding most sugar is the more vigorous.

Lastly, it was a matter of interest to determine whether in other

instances of asphyxia, sugar was also present in the urine. The urine of rabbits which had been strangled and drowned contained sugar; but this was not found to occur in every case, probably because the means for producing the asphyxia entail numerous disturbing causes in the œconomy. Hence a living animal not respiring should yield saccharine urine. M. Bernard has proved that the urine of the fœtus always contains sugar.

M. Reynoso's method of experimenting was this:—The animal or the human subject is first made to pass urine, and then subjected to ætherization. The secretion is collected, treated with basic acetate of lead, filtered, and the excess of the lead salt precipitated with chloride of sodium. The filtered and concentrated liquid is then tested with the alkaline solution of tartrate of potash and copper, or set aside with yeast to produce alcohol and carbonic acid by fermentation.—*Comptes Rendus*, Oct. 20, 1851.

On the Saliva. *By* M. Jacubowitsch.

In regard to the secretion of the saliva, the author's observations show, that the salivary glands continually secrete saliva, whether food has been taken or not. The observation can easily be made upon one's self, that even when no food is taken, motions of deglutition take place at short intervals; and this never occurs without saliva being simultaneously swallowed and conveyed to the stomach. On making a fistulous opening into the stomach of a dog which had previously fasted, a large quantity of liquid was immediately obtained, which had all the appearance of saliva. By means of the microscope, the author satisfied himself, from the presence of a large number of the epithelial cells of the mucous membrane of the mouth, as also from the property possessed by the liquid of converting starch into sugar, which does not belong to the gastric juice, that it really was saliva. Both the secretion and the excretion of the saliva are promoted by psychical and physical excitants. When a piece of meat is presented to a dog which has been kept without food, a large quantity of saliva flows from its mouth, even when no masticatory motions of the lower jaw take place. That the excretion of the saliva is generally promoted by the movements of the lower jaw, was often observed on collecting the secretion of the salivary glands.

Human Saliva, when fresh, is either colourless or bluish, tenacious, and possesses neither odour nor taste. When allowed to stand for a longer or shorter time, it separates into two layers, the uppermost of which is transparent, the lowermost turbid and yellowish-white. The upper clear layer contains cells of pavement-epithelium, and some mucous corpuscles, which are apparently nothing more than epithelial cells not yet perfectly developed. The opake sediment consists of the same cells and mucous corpuscles. The specific gravity of the recently-collected saliva was found to be 1·0026 at 64° F.; that of the clear portion, obtained by allowing the saliva to stand for twenty-four hours, was 1·0023. In Biot's

apparatus, saliva does not produce any rotation of the plane of polarization. When a galvanic current is transmitted through the saliva, a slight coagulum is formed at the negative pole. Saliva always exhibits an alkaline reaction with litmus-paper; the neutral or acid reaction, which some physiologists mention, appears to depend upon morbid conditions of the body. The intensity of the alkaline reaction varies according to whether food has been taken or not. The author's observations upon himself, which extended over a period of four months, showed that in the morning before breakfast it was scarcely perceptible, whilst after this meal it immediately became more distinct. The same relation applies to dinner.

When exposed to the temperature of boiling water, the saliva becomes turbid. Alcohol coagulates it, and throws down white flakes. No change is produced in it by either acetic acid, ferrocyanide of potassium and acetic acid, muriatic, sulphuric, nitric or phosphoric acid, caustic potash or ammonia, or alum. Tannic acid throws down a white flaky precipitate; the same is produced by neutral acetate of lead, which is partly soluble in excess of the precipitant. Basic acetate of lead throws down dense white flakes, which do not redissolve in excess. Solution of iodine containing hydriodic acid colours the saliva red, and throws down yellow flakes. Protochloride of tin produces a white flaky precipitate, insoluble in excess of the precipitant. Peroxide of iron imparts a red colour to the saliva. Protonitrate of mercury throws down dense white flakes, which are partly redissolved on the addition of nitric acid. Bichloride of mercury precipitates whitish flakes, which are not redissolved either on the addition of excess of this reagent or of nitric acid. Sulphocyanide of potassium was detected in it by precipitating a large quantity with alcohol and distilling the filtrate with phosphoric acid. The very acid distillate was neutralized with baryta, and perchloride of iron added, when a deep red colour was produced. The solution was then evaporated, the dried residue heated to redness, and muriatic acid added, when the greater part of the baryta remained as sulphate; another portion of the residue was treated with fuming nitric acid, and then diluted with water, when a large quantity of sulphate of baryta separated.

Numerous experiments were also made upon the saliva and secretion of the mucous membrane of the mouth of the dog. The latter was collected after tying the ducts of the salivary glands. The secretions of the different glands were separately collected by tying those, the secretion of which was not required, and collecting the escaping secretion; and in other experiments tying the latter and collecting the secretion of the former. The results are contained in the following table:—

	Man.	Dog.										
	Saliva.	Saliva, filtered.	Saliva, without the secretion of the parotids, filtered.	Saliva, without the secretion of the submaxillary glands, filtered.	Saliva, without the secretion of the parotids and submaxillary glands.	Secretion of the parotids.	Secretion of the submaxillary glands.	Secretion of the submaxillary glands.	Secretion in one hour from the			
									Mucous membrane of the mouth.	One parotid gland.	One submaxillary gland.	One submaxillary gland.
Water	995·16	989·63	990·48	988·1	990·01	995·3	991·45	996·04	Grms. 24·592	Grms. 24·484	Grms. 25·130	Grms. 13·484
Residue	4·84	10·37	9·52	11·9	9·99	4·7	8·55	3·96	0·248	0·116	0·100	0·116
	1000·00	1000·00	1000·00	1000·00	1000·00	1000·00	1000·00	1000·00				
Analysis of the Residue.												
Epithelium	1·62	.....	.....	2·24								
Organic matter	1·34	3·58	4·33	5·04	.....	1·4	2·89	1·51	.....	0·034	0·038	0·039
Organic matter, soluble in alcohol	.....	.....	.....	.....	1·67	.....	.....	.....	0·042			
Organic matter, insoluble in alcohol	.....	.....	.....	.....	2·18	.....	.....	.....	0·054			
Salts and ash	.....	.....	.....	.....	.....	.....	.....	2·45	.....	.....	0·062	0·077
Phosphate of soda	0·94	0·82										
Chlorides of sodium and potassium	0·84	} 5·82	} 4·00	4·20	5·30	} 2·1	4·50	.....	} 0·132	} 0·052		
Sulphocyanide of potassium	0·06											
Phosphates of lime and magnesia	.....	.....	1·19	0·42	0·84	.....	} 1·16	.....	0·020	0·030		
Carbonate of lime	.....	.....	.....	.....	.....	1·2						
Lime combined with organic matter	0·03	} 0·15										
Magnesia combined with organic matter	0·01											
	4·84	10·37	9·52*	11·9*	9·99	4·7†	8·55	3·96	0·248	0·116	0·100	0·116

* Traces of sulphate of lime.

† Traces of phosphoric acid.

In regard to the organic substances contained in the saliva of the dog, the author concludes that albumen is not present, because the saliva undergoes no change at 212° F. with nitric acid, nor with ferrocyanide of potassium and acetic acid. Moreover, as no scum is formed on its surface on evaporation, and no precipitate is produced by dilute acids and ferrocyanide of potassium, he concludes that it contains no caseine; and that neither pyine, chondrine nor gelatine is present, is proved by acetic acid and alum producing no change, neutral or basic acetate of lead causing no precipitates on evaporation at a gentle heat, and cooling causing no gelatinization.

The other reactions it exhibits show, on the one hand, the presence of mucus, which is secreted by the mucous membrane of the mouth and the submaxillary glands; and indicate, on the other hand, the presence of a substance the nature of which is peculiar, and exists in all the secretions above mentioned, the further study of which the author was unable to pursue on account of the small quantity at his disposal. This is the substance which Berzelius has designated as ptyaline, the salivary matter of Gmelin, the diastase salivaire of Mialhe, and the ptyaline of Wright, and in regard to the chemical reactions of which none of these authors agree perfectly with each other.

By a series of experiments, the author disproves the view lately put forward by Bernard, that the saliva plays no other part in digestion than that of moistening the food, and shows that its function is to digest the starch. He also repeated Wright's experiments, according to which the human saliva exerts a poisonous action upon animals, and refers this effect to poisoning by nicotine, dependent upon the fact that Dr. Wright collected the saliva by smoking tobacco.

The author also disproves the view of M. Bernard, that the formation of sugar from starch by the agency of the gastric juice depended upon the epithelial cells which are suspended in it, by precipitating saliva with alcohol, and filtering the liquid. It was strongly alkaline, and did not exhibit any histological elements under the microscope. When mixed with recently-boiled starch, sugar was formed in ten minutes.

With a view to determine whether the saliva contains a peculiar diastase, some was collected in a fresh state, boiled several times, and mixed with recently-boiled starch. After having been left at a temperature of 100°–104° F. for two hours, it gave no indications of sugar with Trommer's test. But when the starch and the saliva was merely heated to the boiling-point, the ordinary reduction of the peroxide of copper was observed. This experiment therefore excludes the existence of any diastase, which if present would have been deprived of its efficacy by the heat of boiling water.

For the purpose of ascertaining whether other substances, especially acids, might not cause the conversion of starch into sugar, freshly-boiled and also raw starch were mixed with water, also freshly-boiled starch with lactic, phosphoric, acetic, muriatic and nitric acids, and with phosphate of soda and phosphate of lime, and ex-

posed to the same temperature; but after continuing the experiments for twenty hours, in none was any reduction of the peroxide of copper produced. Moreover, to examine whether the alkaline reaction of the saliva had any share in the production of the sugar, some strongly-alkaline saliva was divided into four portions, one of which was neutralized with acetic acid; the second was made acid; to the third was added some very dilute, to the fourth some strong caustic soda. All four of the mixed liquids, after mixture with boiled starch and exposure to a temperature of 100°—104° F. for two hours, reduced the peroxide of copper.

The relation of the gastric juice to the formation of sugar by the saliva was examined as follows:—Some pure filtered gastric juice, obtained from an artificial fistulous opening in the stomach of a dog, which contained no histological elements and was strongly acid, was neutralized with strongly-alkaline human saliva, and mixed with freshly-boiled starch. Another portion of the same saliva was treated with so much of the same gastric juice that the mixture had an acid reaction, and the whole likewise mixed with the starch. Both mixtures, after standing for two hours at a temperature of 100°–104° F., reduced the peroxide of copper.

The following mixtures were also made, and mixed with fresh starch-paste:—*a*. Pure filtered gastric juice was neutralized with human saliva. *b*. The same was rendered alkaline by a large quantity of saliva. *c*. The same was made alkaline with soda. *d*. Saliva was rendered acid by gastric. *e*. Pure gastric was mixed with starch-paste. All these mixtures, excepting *c* and *e*, reduced the copper in fifteen minutes, after digestion at 100°–104° F.

These experiments prove that the gastric juice does not prevent the conversion of starch into sugar by the saliva, and that it is unable to produce this conversion either alone or after neutralization with alkalies.

The author's experiments show, further, that neither the secretion of the parotid, the submaxillary, the sublingual, nor the orbital glands, nor that of the mucous membrane of the mouth, is alone capable of causing the conversion of starch into sugar; nor is this the case with the secretions of the parotid and submaxillary glands when mixed; but that of either of the latter, or both, when mixed with the secretion of the mucous membrane of the mouth, or of the mucous membrane of the nose (which alone does not possess this power), is capable of producing this transformation.

The author states that several constituents of the body, when kept from twenty-four to forty-eight hours, with free exposure to the air, yield a substance which agrees with the saliva in regard to its reaction upon starch. In this way he explains M. Bernard's experiment, in which the prepared mucous membrane of the mouth was found to possess this property.

Further experiments show, that not only does the saliva convert starch into sugar in the body, but that it is essentially requisite to its digestion; moreover, that the formation of sugar within the body is neither occasioned nor prevented by the gastric juice.

The author found, also, that when the pancreatic juice is digested with starch at a temperature of 100°–104° F., the mixture produces a copious reduction of the copper.—*Ann. der Chem. und Pharm.*, vol. lxxix. Heft 2.

On some Constituents of the Root of Aspidium filix mas. *By* Dr. E. Luck.

[Continued from page 438.]

Tannaspidic and Pteritannic Acids.—To prepare these acids, the dried fern root is exhausted with alcohol of 0·875–0·863, and distilled with the addition of one-sixth of the weight of the root of water; the upper smeary layer of the residue is separated from the lower one, the latter diluted with water, some hydrochloric acid added, then some pounded sulphate of soda, and lastly a concentrated solution of sulphate of soda. The precipitate is submitted to strong pressure, the residual cake triturated with water to which a little hydrochloric acid has been added, and digested for about half an hour at a temperature of 140°–176°. It is then washed with water, and dried. The residue is treated with æther free from alcohol until this is no longer coloured by it. The ætherial solution contains the pteritannic acid, the insoluble residue the tannaspidic acid. To purify the latter, the residue is dissolved in hot alcohol, filtered, and the alcohol removed by distillation on the water-bath after the air has been expelled from the retort by means of hydrogen. It is finally dried *in vacuo* over sulphuric acid.

Tannaspidic Acid, $C^{26}H^{13}O^{10}, HO$, an acid which contains 1 equiv. more oxygen and 2 equivs. less hydrogen than filicic acid. When prepared according to the above directions, it forms on pulverization a bright reddish-brown powder, which gives a perfectly clear solution with strong alcohol, but is insoluble in æther and in water. By friction it becomes powerfully electrical. It readily retains bases, on which account it is necessary to use hydrochloric acid in its preparation. A perfectly clear solution of tannaspidic acid leaves, on evaporation at 212° and access of air, a residue which no longer dissolves entirely in alcohol. It is void of smell, and has a slight astringent taste. Placed on the tongue, it somewhat thickens the saliva. It is insoluble in water and in æther, and also in fat oils and oil of turpentine. It dissolves readily in spirit and in absolute alcohol. The spirituous solution has a feeble acid reaction. It dissolves in hot concentrated acetic acid, from which it is again precipitated by the addition of water; it is precipitated for the greater portion from the alcoholic solution by much æther. Heated upon platinum, it burns without residue; in a flask, it first gives off an acid water, disengages an odour resembling that of burnt tartar, and leaves a sparingly combustible cinder. Both in dilute and concentrated caustic potash, as well as in a solution of ammonia, it dissolves with a dark brown colour. In these solutions acids produce flocculent precipitates, which no longer have all the properties of the substance used if the ley was concentrated. If the solution is heated,

it absorbs oxygen, and the liquid acquires a brownish-red colour. When tannaspidic acid is conveyed into boiling solution of caustic potash, it dissolves with a dark brown colour; acids then produce in the solution a black precipitate. When added to fusing nitrate of potash, it turned black. Concentrated sulphuric acid dissolves it with a reddish-brown colour; the liquid appears greenish in thin layers. On the application of heat, it acquires a dark brownish-purple colour; and as this begins at the surface, it appears to be owing to the absorption of oxygen from the atmosphere. Water causes a precipitate in these solutions, but a portion of the substance remains dissolved. With chlorine it furnishes new chlorinated compounds. Tannaspidic acid dissolves in cold fuming nitric acid with a brown colour, and without any disengagement of gas. On the addition of a little water, a precipitate is produced, which again disappears on adding more water. When this aqueous solution is evaporated at a very gentle heat, it leaves a yellow residue, which dissolves in water, strongly reddens blue litmus-paper, and furnishes no precipitate with chloride of calcium; consequently contains no oxalic acid. When the solution in fuming nitric acid is heated, nitric oxide is given off, the colour becomes bright yellow, and water causes no precipitate. When tannaspidic acid is dissolved in ordinary nitric acid and evaporated, it leaves a yellow deliquescent residue, which furnishes a yellow precipitate with lime-water.

When a spirituous solution of tannaspidic acid is boiled with a little hydrochloric acid, a purple-red liquid is obtained, from which water precipitates a red substance. The spirituous solution gives no precipitate with chloride of barium or chloride of calcium; but on the addition of ammonia, a brown precipitate results. Perchloride of iron strikes a green colour, and on the addition of ammonia furnishes an olive-green precipitate. Protochloride of iron gives a grayish-green, with the addition of ammonia a brownish-green precipitate. No opacity is caused by nitrate of silver; but after some time, and immediately on the application of heat, the liquid turns brown. An addition of ammonia causes a heavy kermes-brown precipitate. Bichloride of platinum gives, on the addition of ammonia, a copious brown precipitate; the same is the case with acetate of copper; the latter does not dissolve in an excess of ammonia. Salts of zinc, mercury and tin furnish brown precipitates on the addition of ammonia. A solution of isinglass in weak spirit produces a flocculent precipitate. A solution of tartar-emetic is not precipitated. On analysis, tannaspidic acid furnished—

C.....	60·14	60·16	59·63	60·40	60·90	26	1950	60·46
H.....	5·82	5·77	5·59	5·58	5·51	14	175	5·42
O.....	34·04	33·97	34·78	34·02	33·59	11	1100	34·12

Tannaspidate of Lead, $PbO, C^{26}H^{13}O^{10}$, prepared by precipitating an alcoholic solution of the acid with an alcoholic solution of the acetate of lead, forms when dry a black shining mass, which yields a brown powder. It gave on analysis—

Carbon.....	43·04	26 =	1950	43·26
Hydrogen	3·645	13	162·5	3·60
Oxygen	22·715	10	1000	22·20
Oxide of lead	30·60	1	1394·5	30·94

Dichlorotannaspidic Acid, $C^{26}H^{11}Cl^{2}O^{11}$, is produced, with elimination of heat and production of hydrochloric acid, when a current of dry chlorine is passed over the dry acid to saturation. The product is dissolved in alcohol, and this evaporated by exposure to the air. It forms an amorphous brown substance, which furnishes a cinnamon-coloured powder. It has a peculiar fruity odour, a feeble acid astringent taste; is insoluble in water, æther, fatty and essential oils; it is readily soluble in alcohol; it has a strong acid reaction, and dissolves readily in dilute ammonia and caustic potash with a brown colour. The spirituous solution behaves almost like tannaspidic acid towards metallic salts. The substance, dried *in vacuo*, furnished—

Carbon	47·81	26 =	1950	47·88
Hydrogen	3·35	11	137·5	3·37
Chlorine..... 21·90	..	2	885·2	21·74
Oxygen	25·94	11	1100	27·01

Trichlorotannaspidic Acid, $C^{26}H^{10}Cl^{3}O^{13}$, is formed by passing chlorine into water in which tannaspidic acid is suspended. As soon as the brown colour of the powder is converted into a pale brown, it is dried, dissolved in alcohol, and the solution evaporated. The new acid is amorphous, insoluble in water, æther, fat and essential oils, readily soluble in alcohol, and has an acid astringent taste, with a peculiar odour similar to that of the preceding compound; it strongly reddens blue litmus-paper. The spirituous solution produces a copious caseous precipitate in a solution of gelatine. It dissolves easily in alkaline liquids, with a yellowish-brown colour. It gives a brown precipitate with chloride of barium and chloride of calcium after the addition of ammonia, a bright green with protochloride of iron, a brownish-green with peracetate of iron, a yellowish-green with acetate of copper, and a brown with protochloride of tin; it causes no opacity in nitrate of silver or in bichloride of platinum; it does not dissolve in cold sulphuric acid; on the application of heat, it blackens. Solution of potash dissolves it with a brown colour, which when heated becomes darker. It gave on analysis—

Carbon	41·27	26 =	1950	41·46
Hydrogen	2·69	10	125	2·65
Chlorine.....	28·13	3	1327	28·23
Oxygen	27·91	13	1300	27·66

Trichlorotannaspidate of Lead, $PbO, C^{26}H^{10}Cl^{3}O^{13}$, is obtained by precipitating a solution of the acid in alcohol with acetate of lead in the form of a brown flocculent precipitate, which forms when dry a blackish-brown shining mass. It gave—

Carbon	31·75	26 =	1950	31·98
Hydrogen	2·11	10	125	2·05
Chlorine	..	3	1327·9	
Oxygen	..	13	1300	
Oxide of lead	22·10	1	1394·5	22·78

Trichloroxytannaspidic Acid, $C^{26}H^{10}Cl^{3}O^{14}$, is formed when tannaspidic acid is gently heated with dilute hydrochloric acid with the addition of pieces of chlorate of potash. It is a fiery orange-yellow powder, which is slightly soluble in the warm mother-liquor, insoluble in water, and readily soluble in alcohol, which leaves it on evaporation as an amorphous mass. The solution has a strong acid reaction; the taste is somewhat astringent. Towards metallic salts it behaves like the preceding acid. On analysis it furnished—

Carbon	40·39	26 =	40·39
Hydrogen	2·90	10	2·90
Chlorine	27·33	3	27·33
Oxygen	29·16	14	29·38

Trichloroxytannaspidate of Lead, $PbO, C^{26}H^{10}Cl^{3}O^{14}$, obtained by adding acetate of lead to an alcoholic solution of the acid, is a flocculent precipitate of the following composition :—

Carbon	31·44	26 =	1950	31·46
Hydrogen	2·18	10	125	2·01
Chlorine	..	3	1327·9	
Oxygen	..	14	1400	
Oxide of lead	22·30	1	1394·5	22·50

Tetrachloroxytannaspidic Acid, $C^{26}H^{9}Cl^{4}O^{13}, 3HO$, is formed when moist chlorine is passed over air-dried tannaspidic acid to saturation; heat is evolved, and hydrochloric acid formed; it has a darker colour than the preceding compound, a similar odour, but a very slight taste; it dissolves readily in alcohol and alkaline liquids with a brown colour. The reactions with metallic salts are almost the same as in the case of trichlorotannaspidic acid. It gave on analysis—

Carbon	35·74	26 =	1950	35·61
Hydrogen	2·81	12	150	2·73
Chlorine	32·12	4	1770·5	32·33
Oxygen	29·33	16	1600	29·33

Iodine also acts upon tannaspidic acid, separating hydrogen in the form of hydriodic acid, and replacing it.

Æthylotannaspidic Acid, $2C^{26}H^{13}O^{10} + C^{4}H^{5}O$.—When tannaspidic acid is boiled with alcohol and some hydrochloric acid, the solution acquires a purple-red colour. Water precipitates from this solution a red substance free from chlorine, which dissolves easily in alcohol, and furnishes with acetate of lead a beautiful bluish-green precipitate. The red precipitate is washed with water, and dried at a gentle heat; in alcohol it dissolves with a very deep purple colour. On careful evaporation, which is best effected *in vacuo* over sulphuric acid, the acid is left as a shining, amorphous, dark purple

substance. All the derivatives of tannaspidic acid are characterized by their ready solubility in alcohol and insolubility in æther, whereby they differ from pteritannic acid and its derivatives, which are all soluble in æther. This compound furnishes, with potash, soda and ammonia, green combinations when not decomposed by them. Litmus is scarcely reddened by its solution; dilute nitric acid converts it into a brownish-red substance; sulphuric acid dissolves it with an orange-brown colour. When exposed for any length of time to the air, the colour becomes turbid and brownish; this quickly happens on desiccation at 212°; it must therefore be dried *in vacuo* over sulphuric acid. On analysis it furnished—

Carbon	62·92	56 =	4200	62·81
Hydrogen	5·79	31	387·5	5·79
Oxygen	31·29	21	2100	31·40

The author is of opinion that the oxide of æthyle is not combined in the usual manner, but exists in it rather as a conjunct, as it behaves more like an entire organic group. With alumina and protochloride of tin it furnishes a lake like a pigment. The recently-prepared alcoholic solution gives, with chloride of barium and chloride of calcium, no precipitate until after the addition of some ammonia. Protochloride of iron and peracetate of iron furnish a copious greenish-black, acetate of copper a brownish-violet precipitate. Nitrate of silver and bichloride of platinum are not rendered turbid. On the addition of ammonia a dark brown precipitate results with the first, and with the latter a dark violet. Chloride of aluminium causes a violet colour, and on the addition of ammonia a very beautiful precipitate of the same colour; protochloride of tin furnishes a violet-red precipitate; acetate of lead and basic acetate of lead give copious beautiful green precipitates, which however soon turn bluish-green, inclining to gray. A solution of gelatine is rendered somewhat turbid. Sulphuretted hydrogen causes no discoloration; chlorine instantly destroys the compound.

Æthylotannaspidate of Lead, $2C^{26}H^{13}O^{10} + C^4H^5O$, PbO, is the beautiful dark green precipitate which acetate of lead throws down from a recently-prepared solution of the æthylotannaspidic acid in alcohol. It furnished on analysis—

Carbon	51·99	56 =	4200	51·97
Hydrogen	4·73	31	387·5	4·79
Oxygen	26·03	21	2100	25·99
Oxide of lead	17·25	1	1394·5	17·25

Basic acetate of lead precipitates from the solution of the acid a compound containing 31·08 oxide of lead, which amount corresponds to the formula $2C^{26}H^{13}O^{10} + C^4H^5O$, 2PbO.

[To be continued.]

On a new Photographic Process. *By* Mr. C. J. Muller.

The following photographic process has been communicated to us by Mr. C. J. Muller, from Patna in the East Indies. We have

submitted it to an experienced photographer; and he informs us that it offers many advantages over the Talbotype or the Catalisso-type of Dr. Woods, which it somewhat resembles, that it is easy in all its manipulatory details, and certain in its results. We give Mr. Muller's own words:—

"A solution of hydriodate of iron is made in the proportion of 8 or 10 grs. of iodide of iron to 1 oz. of water. This solution I prepare in the ordinary way with iodine, iron-turnings and water. The ordinary paper employed in photography is dressed on one side with a solution of nitrate of lead (15 grains of the salt to an ounce of water). When dry, this paper is iodized either by immersing it completely in the solution of the hydriodate of iron, or by floating the leaded surface on the solution. It is removed after the lapse of a minute or two, and lightly dried with blotting-paper. This paper now contains iodide of lead and protonitrate of iron. While still moist, it is rendered sensitive by a solution of nitrate of silver (100 grs. to the ounce), and placed in the camera. After an exposure of the duration generally required for Talbot's paper, it may be removed to a dark room. If the image is not already out, it will be found speedily to appear in great strength and with beautiful sharpness, *without any further application.* The yellow tinge of the lights may be removed by a little hyposulphite of soda, though simple washing in water seems to be sufficient to fix the picture The nitrate of lead may be omitted; and plain paper only, treated with the solution of the hydriodate of iron, and acetic acid may be used with the nitrate of silver, which renders it more sensitive. The lead however imparts a peculiar colorific effect. The red tinge brought about by the lead may be changed to a black one by the use of a dilute solution of sulphate of iron, by which indeed the latent image may be very quickly developed. The papers however will not keep after being iodized."

Mr. Muller suggests, that as iodide of lead is completely soluble in nitrate of silver, it might furnish a valuable photographic fluid, which could be applied at any moment when required.

It appears perfectly applicable to the albuminized glass and collodion processes.—*Athenæum*, Nov. 22, 1851.

√ *On the Deportment of Water towards the Carbonic Acid in the Carbonates of the Protoxide of Manganese and Oxide of Lead. By* Prof. H. Rose.

Combinations of Carbonic Acid and Water with the Protoxide of Manganese.—Water expels less carbonic acid from the protocarbonate of manganese than from many other carbonates. By decomposing solutions of equivalents of protosulphate of manganese and carbonate of soda, a compound consisting of 5 atoms of protoxide of manganese with 1 atom of the hydrate of the protoxide is most frequently formed; for of eleven precipitates examined, four contained such a proportion between the carbonic acid and protoxide

of manganese as would correspond to such a compound. Some of the compounds of the protocarbonate of manganese with the hydrate of the protoxide absorb at 212° a very small quantity of carbonic acid from the atmosphere, as is the case with several of the combinations of the carbonate of magnesia with the hydrate.

When the compounds are heated to 300°, they gradually become dark brown. The protocarbonate remains unaltered, but the hydrate of the protoxide is oxidized into hydrated sesquioxide. At 392° the protocarbonate is likewise converted into hydrated sesquioxide.

Combinations of Carbonic Acid and Water with Oxide of Lead.—Formerly the precipitate which is obtained from solutions of soluble lead salts with a neutral alkaline carbonate was regarded as neutral carbonate of lead; it however contains water, although only in small quantity, and less carbonic acid than is required to form a perfectly neutral compound. When solutions of equivalents of nitrate of lead and carbonate of soda are mixed, the compound $6PbO, CO^2 + PbO, HO + HO$ is obtained from concentrated cold solutions; at 392° it parts with water, and absorbs carbonic acid; with dilute cold solutions the compound $5PbO, CO^2 + PbO, HO$ is formed, which is likewise obtained from concentrated hot solutions; from dilute hot solutions, on the contrary, the compound $3PbO, CO^2 + PbO, HO$ falls. When a solution of the nitrate of lead is precipitated with an excess of carbonate of soda, the precipitate contains some soda; but it is essentially $2PbO, CO^2 + PbO, HO$, which compound, according to the experiments of Mulder and Hochstetter, is likewise principally formed in the preparation of white lead.—*Bericht der Berlin Acad.*, 1851, p. 597.

ANALYTICAL CHEMISTRY

On the Estimation of Iodine. By MM. GRANGE *and* LASSAIGNE.

ACCORDING to M. Grange, the iodine, after having been set free by nitric or sulphuric acid or chlorine, can be taken up by sulphuret of carbon, which thereby acquires a violet colour; or by chloroform, which assumes the same colour, only fainter. When bromide of potassium is treated in the same manner, both these solvents are coloured orange; they also both dissolve chlorine with a yellowish-green colour. $\frac{1}{100}$dth of a milligramme of iodide of potassium dissolved in 1 cub. centim. of water still imparts a colour to chloroform and sulphuret of carbon.

Chloroform was recently proposed for detecting iodine by Rabourdin. According to M. Grange, it is requisite to use great precaution when bromine and sulphurets occur at the same time. When bromine is present, it hides the reaction of chlorine and

iodine; the chloroform assumes a yellow colour, and it is no longer possible to tell from its appearance whether it arises from iodine, chlorine or bromine; and lastly, the least trace of sulphuret completely destroys the reaction of all three.

M. Grange finds, as observed by Dr. Price, that nitrous acid (which must be free from nitric acid) may be used to detect iodine. Bromide of potassium is not decomposed by it, whilst the same acid liberates iodine from its combinations. M. Grange uses nitrite of potash, and decomposes it by very dilute hydrochloric acid; in this manner he discovered iodine in the water of the Seine and various well-waters, in which it could not be detected by any other means.

When all three, chlorine, iodine and bromine, are present at the same time, the iodine is first set free by means of nitrous acid, and extracted with chloroform, which is decanted and washed; then the bromine is liberated by means of nitric and sulphuric acids, and this also extracted by chloroform, after which the chlorine is determined by nitrate of silver; the amount of bromine is also ascertained by a solution of silver. The iodine is determined by nitrate of silver or chloride of palladium, or by comparison of the coloured chloroform solution with prepared solutions of iodine in chloroform of known strength.

M. Lassaigne makes the following observations respecting the methods of detecting iodine:—If, according to Rabourdin, only one hundred-thousandth of iodine can be detected by chloroform, this reagent is less sensitive than starch, since a four-times less quantity can still be demonstrated by starch, and dissolved starch will even show by its blue colour one hundred-millionth of iodine. Twelve years ago Lassaigne recommended chloride of palladium as a test for iodine. He now finds that 2 litres of water, containing two-millionths of iodide of potassium, is still distinctly coloured brown by chloride of palladium. After twenty-four to thirty-six hours, a flocculent sediment of iodide of palladium was formed. If there be but few flakes, a little fine silica is added after the water is poured off, the sediment collected, dried, and then heated in a little glass tube, which becomes filled with vapours of iodine.—*Journ. de Pharm. et de Chim.*, xix. p. 425.

Blowpipe Test for Sulphur. *By* James D. Dana.

The test for sulphur by means of the nitro-prusside of soda is suggested by Prof. J. W. Bailey in this Journal, p. 379. The following are more minute directions for the use of this elegant test:—

Heat by blowpipe any sulphuret or sulphate (or anything containing sulphur) upon charcoal with carbonate of soda, put the fused mass into a watch-glass with a drop of water, and add a particle not larger than a pin's head of the nitro-prusside of soda; there will be a magnificent purple at once. If this test for sulphur is tried upon parings of nails, hair, albumen, &c., I would advise that the carbonate of soda be mixed with a little starch, which ap-

pears to prevent the loss of any of the sulphur by oxidation. If you wind up a piece of hair four inches long by coiling it around one point of a platinum support, then moisten it and dip it into the mixture of carbonate of soda with starch, and then heat by blowpipe, the fused mass will give with the nitro-prusside an unmistakeable action indicative of sulphur. This experiment any one can repeat. By careful management I obtained perfectly satisfactory results from a piece of hair less than an inch long.—Silliman's *Journal*, November 1851.

Test for the soluble Constituents of the Gums.
By J. L. Lassaigne.

The so-called gums are complex natural products. In certain kinds two substances have been distinguished,—the one arabine, soluble in cold water; the other cerasine, insoluble therein. The former constitutes the greater portion of gum-arabic and Senegal gum, whilst the latter predominates in cherry-gum and gum-tragacanth.

For such gums as consist entirely or partially of arabine, the author recommends the persulphate of iron and tribasic acetate of lead as tests.

The sulphate of iron precipitates the gum even from solutions of sugar, which has no influence upon the precipitate; this is yellowish, gelatinous and transparent. This result deserves especial attention, as there are other substances soluble in water, which are precipitated by alcohol and basic acetate of lead, but upon which the sulphate of iron has no influence. The precipitate produced by the lead salt and alcohol is liable to be confounded with dextrine, and other gum-like substances, which so frequently occur among vegetable products; the salt of iron distinguishes arabine from these decidedly.

The soluble portion of gum-tragacanth, which is regarded as isomeric with arabine, is precipitated, like arabine, by the sulphate of iron; but the precipitate by tribasic acetate of lead is white, flocculent, opake and caseous, whilst the gum extracted from tragacanth with cold water furnishes a transparent gelatinous precipitate with basic acetate of lead.

In syrup mixed with gum-arabic the gum can be detected by sulphate of iron in the portion precipitated by alcohol. Dextrine, the gummy constituent which alcohol throws down from commercial starch-syrup, does not furnish with sulphate of iron a precipitate like arabine, so that an admixture of gum is easily detected. —*Journ. de Chim. Méd.*, vii. p. 580.

THE CHEMICAL GAZETTE.

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SCIENTIFIC AND MEDICINAL CHEMISTRY.

On the Atomic Weight of Ozone.
By MM. Osann *and* Schönbein.

Osann has published the results of some experiments upon ozone, from which he concludes that ozone and oxygen have different atomic weights. Lead compounds served for the comparative examination. Acetate of lead was precipitated by carbonate of soda, and the carbonate of lead dissolved in nitric acid. The solution was evaporated to crystallization, the crystals obtained again dissolved, the solution evaporated, and placed aside to crystallize. The crystals first formed were taken out, and preserved for subsequent use. They were dissolved in water, and precipitated by ammonia. The hydrated oxide of lead obtained was placed upon two filters. After both precipitates had been washed, the one was boiled in caustic soda, and the other decomposed by heat, and thus converted into oxide. The oxide of lead thus obtained was free from carbonic acid. It was dried by means of a special arrangement, the moisture estimated, and a determination of the atomic weight made by reducing the pure oxide by hydrogen. The results gave for the composition of 100 parts of oxide, after deducting the water—

1.	92·93 lead	7·07 oxygen
2.	92·90 lead	7·10 oxygen
Mean	92·91 lead	7·09 oxygen,

from which it would follow that the atomic weight of lead would be 104·83.

Ozone-oxide of lead was now prepared by the hydro-electrical method. A small bottle was filled very nearly to its mouth with a mixture of 1 part distilled sulphuric acid and 6 parts of distilled water; two strips of platinum passing through the stopper of glass dipped into the liquid in one direction, and projected beyond the stopper on the other, terminating in small glass tubes containing mercury. By this means the two strips of platinum might be connected with a small Grove's battery. One end of a twice-bent glass tube passed through the stopper; the other end dipped into a bottle containing water, also closed by a stopper; and from which a second glass tube passed into a small Woulf's bottle, filled with the solution of oxide of lead in caustic soda. In the second opening of the

Woulf's bottle was a glass tube, the extremity of which dipped into water. The solution was thus entirely shut off from the influence of atmospheric air. The hydrogen and ozone-oxygen gases evolved by the electrolysis were compelled to pass through the solution of oxide of lead in caustic soda, and could thus act upon the oxide of lead. A yellow deposit was formed of ozone-oxide of lead, which was collected and washed. This precipitate was analysed in the same manner as the former, and the water which the precipitate lost by perfect drying was also estimated. After deducting the water, numbers indicating the following composition were obtained:—

1.	89·38 lead	10·62 ozone-oxygen
2.	89·67 lead	10·33 ozone-oxygen
Mean	89·52 lead	10·48 ozone-oxygen.

From his previous investigations*, Osann came to the conclusion, that the ozone-oxide of silver consisted of 93·28 silver and 2·72 ozone-oxygen. If the atomic weight of ozone is deduced from these numbers, as well as from the above lead compounds, corresponding results are obtained:—

Pb = 103·74	Atomic weight of ozone = 6·04
Ag = 108·15	Atomic weight of ozone = 6·07

Osann is of opinion that ozone cannot be an allotropic modification of oxygen. He considers that a peculiar atomic weight and specific weight are sufficient reasons for no longer admitting one body to be a mere modification of another. Perhaps ozone-oxygen is the definite compound OH^2, upon the assumption that the atomic weight of oxygen is to be taken as only half the usual value, viz. 4. According to Osann, ozone does not present the characters which oxygen does at the instant of separation. As formic acid is converted into carbonic acid when it or its salts are brought into contact with oxygen in the nascent state, ozone-oxygen was passed through formic acid, and afterwards through an aqueous solution of formiate of lime. However, no alteration of the acid took place.

Osann then proceeds to some other experiments, from the results of which he concludes that the first atom of oxygen in hyperoxides has the atomic weight 8, the second being ozone-oxygen having the atomic weight 6·10. Schönbein had already distinguished between the two atoms of oxygen in a similar manner, by writing the formula of hyperoxides $MO+O^0$ instead of MO^2, but he did not arrive at such differences in the atomic weights. Pure peroxide of silver was prepared by the hydro-electrical method from acetate of silver. After sufficient washing, it was dried, and a small quantity reduced by the action of hydrogen and heat; the water obtained had no acid reaction. This oxide of silver shaken with solution of guaiacum gave a blue colour immediately.

Oxide of manganese, powdered and washed, reduced by hydrogen gas and heat, gave water which had no acid reaction. If the peroxide is shaken with guaiacum-solution, it assumes a blue colour. If a drop of an alcoholic solution of guaiacum is placed upon the

* Chem. Gaz. vol. viii. p. 25.

above-mentioned ozone-oxide of lead, a blue colour is immediately produced. If, on the contrary, ordinary oxide of lead, obtained by heating carbonate of lead, is rubbed upon paper, and afterwards moistened with guaiacum-solution, no blue colour is produced. Red lead, rubbed upon paper, and moistened with guaiacum-solution, assumes a very feeble blue colour. The author infers from these facts, that the blue colouring produced with guaiacum-solution must depend upon the second atom of oxygen, and that this must be ozone-oxygen. But if this second atom of oxygen in the peroxide be ozone-oxygen, it must also have an atomic weight expressed by 6, or some value very near to that. The peroxide of lead employed in these experiments was prepared by the action of acetic acid upon red lead. The hygroscopic moisture was quantitatively estimated as before. The peroxide was heated until it was converted into yellow oxide, and the loss of weight found to correspond with the atomic weights:—

1.	6·08	3.	6·26	
2.	5·63	4.	6·13	Mean = 6·10

This atomic weight agrees well with that deduced from the more simple compounds of oxide of silver and oxide of lead. The author also attempted to determine the specific weight of the oxygen gas, which was obtained by heating the peroxide of lead. The gas was collected in a graduated tube over mercury. The results obtained were, that 1 cub. centim. of the gas at 32° F. and $0^{m}{\cdot}76$ weighed 0·0013 gr. The ordinary determination gives as the weight of a cubic centimetre 0·0012 gr. There is therefore no difference in specific gravity. Accordingly the author, after having already expressed himself opposed to the opinion of an allotropic modification, finally comes to the conclusion that ordinary oxygen is the thermic modification, ozonized the electric modification of oxygen. The latter can be converted into the former by heat, and on this account the gas evolved from the hyperoxides by heat is not ozone-oxygen. It is not improbable that the marked electro-negative character of the hyperoxides is occasioned by the electric modification of oxygen, *i. e.* the ozone-oxygen.

Schönbein opposes the principal views expressed by Osann. According to his own experiments, silver is converted by means of ozone into a peroxide, of which 100 parts afford by heating 87 per cent. of metal and 13 per cent. of oxygen, a proportion which agrees well with the formula AgO^{2}, assigned to the peroxide of silver. This fact shows that the ozone combines with silver in the same proportion in which ordinary oxygen enters into combination with other elements. But the oxide of silver shows the same behaviour with guaiacum-tincture as the peroxide of lead; consequently it may be assumed that O^{o}, that is ozonized oxygen, is present in the one as well as in the other. In addition to this, the accurately analysed basic oxide of silver (AgO) gives as decided a blue colour with tincture of guaiacum as peroxide of lead does; it must consequently be assumed that ozonized oxygen is also pre-

sent in oxide of silver. Moreover, the composition of the peroxide of manganese is known with sufficient accuracy to enable us to say that it does not contain an atom of oxygen, having the atomic weight 6. Again, by means of ozone at an ordinary temperature, a number of simple and compound bodies may be oxidized, for example, phosphorus to phosphorous and phosphoric acids, nitrogen to nitric acid, metallic arsenic to arsenic acid, sulphurous acid to sulphuric, sulphuret of lead to sulphate, &c. And these compounds formed by ozone are perfectly similar to those which are obtained by oxidating agents. Schönbein therefore considers the existence of oxygen having the atomic weight 6 as inadmissible.—Poggendorff's *Annalen*, vol. lxxxii. pp. 531–544; *Journ. für Prakt. Chem.*, vol. liii. pp. 248–252.

On the Gastric Juice. *By* M. Hübbenet.

The gastric juice was collected by means of a fistulous opening in the stomach, the salivary ducts being at the same time tied, or portions of them cut out, and the wound allowed to heal. The experiments were made upon dogs and a sheep. The aspect and composition of the gastric juice were found to vary according to the quantity and quality of the food. When animal food was taken, it was more yellow in colour; when the food consisted of hay, it was of a dark brownish colour. It is always acid. In regard to the cause of the acid reaction, the author adopts the view of M. Schmidt, according to which it arises from a conjugate compound of muriatic acid with an organic ferment. The analyses of the gastric juice, as performed by M. Schmidt, are quoted. He found in 1000 parts of the—

	Gastric juice of a dog (not mixed with saliva), A*.	Gastric juice of a dog (mixed with saliva), B†.	Gastric juice of a sheep‡.
Water	973·062	971·171	986·147
Dry residue	26·938	28·829	13·853
Ferment	17·127	17·336	4·055
Muriatic acid	3·050	2·337	1·234
Chloride of potassium	1·125	1·073	1·518
Chloride of sodium	2·507	3·147	4·369
Chloride of calcium	0·624	1·661	0·114
Chloride of ammonium	0·468	0·537	0·473
Phosphate of lime	1·729	2·294	1·182
Phosphate of magnesia	0·226	0·323	0·577
Perphosphate of iron	0·082	0·121	0·331
	26·938	28·829	13·853

The amount of free acid was determined by filtering the gastric fluid, and neutralizing with potash. It was found remarkably greater in the dog B, the gastric juice of which was mixed with the saliva, than in that of A, in which this was not the case; whilst the

* Mean of ten analyses. † Mean of three analyses. ‡ Mean of two analyses.

analysis shows that the quantity of muriatic acid in the gastric juice of the dog A is greater than in that of the dog B. It would thus appear as if that the starch in the stomach of the dog B had been converted by the saliva into sugar, dextrine, and finally lactic acid, but no trace of sugar could ever be detected in its stomach.

The author found that the gastric mucus was only secreted when the animals had been long kept without food. No gastric epithelial elements could be found in this mucus. The mucus was neutral, except in one case, in which it was found alkaline. Experiments were made out of the body, with the filtered and not filtered gastric juice, with that which was acid, and the same after neutralization; also when rendered alkaline, further with the boiled and evaporated gastric juice. The boiled white of eggs, cut into cubes, was used as the standard of the digestive powers. Each of these was weighed; one of them was then dried and again weighed; the others were used for the experiments, being digested with the digestive liquid, then removed from it, dried, and again weighed. The weight of the dried substance was then compared with the portion dried before the experiment, and so the loss in weight determined per cent. The results of the experiments are tabulated below:—

	Gastric juice.								Muriatic acid.
	Number of experiment.	Duration of experiment.	Liquid used.	Was neutralized by p. c. of potash.	Acid.	Neutral.	Alkaline.	Boiled, acid.	Loss in weight of the white of egg.
					Loss in weight of the white of egg.				
		hours.	grms.		p. c.	p. c.	p. c.	p. c.	p. c.
Dog A	1	19	6	0·19	*24·31	6·62	3·55		
„	„	„	„	„	25·90	4·58	6·64		
„	2	18	5	0·39	*56·61	*7·23	*2·44		
Dog B	3	20	6	0·17	*26·87	*4·64	*11·45		
„	„	„	„	„	29·09	2·65	16·53		
„	4	21	5	0·42	...	9·85	...	...	8·40
„	5	20	6	0·33	50·48	16·17	11·32		
„	„	„	„	„	*55·85	*16·30	*6·57		
„	6	21	5	0·44	*75·21	11·61	...	...	15·20
„	7	22	5	0·28	*19·83	7·49	...	5·43	
„	8	20	5	0·28	*26·35	...	...	5·93	10·69
Dog C	9	20	5	...	*14·31	...	3·16		
				Mean	36·80	8·71	7·70		
Sheep	5	20	5	0·28	*15·72	*15·75			
„	6	21	5	...	*21·83				
„	„	„	„	...	9·18				
„	10	23	5	...	...	...	...	2·02	
Dog B	„	„	„	...	...	...	...	9·36	
Experiment with Meat.									
Dog A	11	18	4·1	...	*60·38	...	52·96		

* Filtered.

Besides the experiments in the table, the following were made:—

To Experiment 2.—5 grms. of alkaline mucus, diluted with the same quantity of water. The loss in weight amounted to 19·62 per cent.

Mucus acidified with muriatic acid. Loss in weight of the white of egg, 29·14 per cent.

To Experiment 4.—Gastric juice boiled to one-sixth of its volume, diluted with an equal volume of water. This experiment gave an *increase of weight in the white of egg* =0·41 per cent.

To Experiment 6.—Gastric juice evaporated at a gentle heat to one eighth of its volume, diluted with as much water. *Increase in weight* =21·85 per cent.

To Experiment 8.—Gastric juice neutralized with 1·25 grm. of bile. *Increase of weight* =9·14 per cent.

Experiments were then made in the body, by introducing the coagulated white of egg through the fistulous opening into the stomach. The results are given in the table.

Of 100 parts of white of egg there were dissolved—

Duration of the experiment.	Dog A (without saliva) in			Dog B (with saliva) in			Sheep in			
	2 hours.	4 hours.	6 hours.	2 hours.	4 hours.	6 hours.	2 hrs.	4 hrs.	6 hrs.	22 hrs.
1	51·84	87·19	86·61	34·94	69·09	93·37	21·54	24·45	...	89·88
2	29·50	60·28	78·61	...	...	96·10	23·90	44·50	55·32	
3	41·02	78·02	92·49	21·12	50·14	78·52	5·63	28·13	32·01	
4	13·20	54·84	77·75	...	...	50·17				
5	52·83	72·18	75·03	26·27	48·74	56·15				
6	24·27	42·00	68·51	24·45	42·49	61·71				
7	30·65	80·36	77·84	28·93	29·15	39·32				
8	37·77	59·70	92·32	26·36	37·72	54·16				
9	5·79	29·25	35·66	16·58	40·46	59·51				
Mean	29·54	62·64	76·08	26·95	45·44	65·44	17·02	32·36	43·66	89·88
10	...	...	...	2·48	4·83	20·29				
...	...	...	...	...	...	14·94				
11	...	...	...	3·57	8·09	24·05				

The author draws the following conclusions from the above experiments:—

The acid gastric juice possesses a peculiar property of dissolving white of egg. This property is not altered by filtering the gastric juice; hence it is not probable that, as Frerichs supposes, it depends upon the presence of cells. (See the first table.)

This power is greater or less according to the larger or smaller quantity of muriatic acid conjugated with an organic matter present. (See the second table, and the analyses of the gastric juice of the two dogs.)

This power is destroyed by boiling or evaporating the gastric juice, and is diminished by neutralizing it with potash.

The neutral or alkaline gastric mucus does not dissolve the white

of egg, but appears to obtain this power to a slight extent by the addition of muriatic acid.

The author found, in the case of the dog A, that no sugar was formed on digesting starch with the gastric juice or mucus, either within the body for twenty-two hours or without, although starch-paste, when exposed alone to the air and heat, frequently yields sugar even at the end of twelve hours.

Experiments were also made after dividing the nervi vagi, from which the author draws the following conclusions:—

1. The spontaneous motions of the stomach do not cease.

2. No pathological change is found to ensue in the stomach at the end of fifty to seventy-five hours.

3. No important alteration in the quantity of the gastric juice occurs.

4. The chemical composition of the gastric juice, excepting in one instance the presence of a larger quantity of muriate of ammonia, is not essentially altered.

5. After the division of the nerves, the white of egg is dissolved; but its solution requires a longer time than before.

6. As appeared from the symptoms following the operation, the animals fell into a state of strong fever.—*Ann. der Chem. und Pharm.*, August 1851.

On some Constituents of the Root of Aspidium filix mas. *By* Dr. E. Luck.

[Concluded from page 456.]

Pteritannic Acid, $C^{24}H^{14}O^{7}$, HO.—It has already been stated how the solution of the crude acid in æther is obtained. The æther is removed, the residue exhausted with rectified naphtha, the insoluble residue again dissolved in æther, and the æther distilled off, when adherent naphtha is removed. The acid is then left as a blackish-brown, amorphous, shining substance, which furnishes a fawn-coloured, somewhat reddish powder. When rubbed to powder, it very easily becomes electrical. It is tasteless, and has a feeble peculiar odour. It is readily soluble in æther and strong alcohol, less so in weak spirit, insoluble in water, oil of turpentine, naphtha and fatty oils; the spirituous solution slightly reddens blue litmus-paper. A solution of gelatine gives a flocculent precipitate. In sulphuric acid it dissolves with a yellowish-brown colour, and on the application of heat the solution turns reddish-brown; solution of potash dissolves it with a brown colour; when heated, the solution turns brownish-red, with absorption of oxygen. The spirituous solution gives no precipitate with chloride of barium and chloride of calcium; but on the addition of some ammonia, a brown precipitate results. Proto- and perchloride of iron give green precipitates; acetate of copper, nitrate of silver, chloride of platinum and chloride of aluminium behave as with tannaspidic acid; nitric acid converts it into a yellowish-brown substance; it is also oxidized by

exposure to the air, but far more slowly than is the case with tannaspidic acid. Heated upon platinum, it melts at a gentle heat, gives off balsamic vapours, and burns with a luminous flame, leaving behind a shining cinder. It gave on analysis—

Carbon	64·41	24	= 1800	64·57
Hydrogen	6·90	15	187·5	6·72
Oxygen	28·69	8	800	28·71

Lead Salts of Pteritannic Acid.—When a solution of the pteritannic acid is precipitated with acetate of lead, avoiding an excess of the latter, a grayish-brown precipitate, I., is formed, which has the composition $PbO, HO + 2C^{24} H^{14} O^7$, and is consequently an acid salt. An excess of the neutral acetate or the basic acetate of lead gives a lighter-coloured precipitate, II., represented by $PbO, C^{24} H^{14} O^7$; on mixing some ammonia with the mother-liquor of the latter salt, a light fawn-coloured precipitate falls, III., which is the basic salt $3PbO, HO, 2C^{24} H^{14} O^7$. These salts gave on analysis—

	I.		II.			III.		
C	52·47	48 =	52·50	44·07	24 =	44·22	37·82	48 = 37·32
H	5·31	29	5·28	4·31	14	4·30	3·98	29 3·75
O	22·12	15	21·89	17·52	7	17·22	14·75	15 15·56
Pb O..	20·10	1	20·33	34·10	1	34·26	43·45	3 43·37

Trichloropteritannic Acid, $C^{24} H^{12} Cl^3 O^8$, prepared by treating dried pteritannic acid in a current of dry chlorine, is an orange-brown powder, of a peculiar faint odour and somewhat bitter taste. Heated upon platinum, it melts, and gives off acid fumes. It is insoluble in water and oils, readily soluble in æther and strong alcohol; in alkalies it dissolves with a brown colour. The spirituous solution strongly reddens blue litmus-paper. The proto- and perchloride of iron are precipitated dirty green, acetate of lead brown, chloride of copper yellowish-brown. The chlorides of calcium and barium, and nitrate of silver are not precipitated. Solution of gelatine is only rendered slightly turbid, tartar-emetic not at all. Analysis gave—

Carbon	44·13	24	= 1800	44·14
Hydrogen	3·91	12	150	3·67
Chlorine	19·77	3	1327·9	19·63
Oxygen	32·19	8	800	32·56

Trichloropteritannate of Lead is produced by precipitating the spirituous solution of the acid with basic acetate of lead. The precipitate contains 25·48 per cent. oxide of lead.

Dichloropteritannic Acid, $C^{24} H^{13} Cl^2 O^8, HO$, is formed by passing chlorine into water in which pteritannic acid is suspended. The product is washed with water, and dissolved in æther; when this evaporates, an amorphous residue is obtained, which furnishes a bright loam-coloured powder of a faint, agreeable, fruity odour, and scarcely any taste. It is insoluble in water, fatty and essential oils, but dissolves in æther and in alcohol. The spirituous solution behaves exactly like trichloropteritannic acid towards the per- and protochlo-

ride of iron, gelatine, nitrate of silver, chloride of barium, &c. It furnished on analysis—

Carbon	47·54	24 =	1800	47·87
Hydrogen	4·80	14	175	4·65
Chlorine.....	23·33	2	885	23·54
Oxygen	24·33	9	900	23·94

Dichloropteritannate of Lead, $PbO, C^{24} H^{13} Cl^2 O^8$, obtained by precipitating the alcoholic solution of the acid with basic acetate of lead, gave—

Carbon	35·85	24 =	1800	35·70
Hydrogen	3·23	13	162·5	3·22
Chlorine.....	..	2	885	
Oxygen	..	8	800	
Oxide of lead	27·63	1	1394·5	27·66

Æthylopteritannic Acid, $C^4 H^5 O, HO, 2C^{24} H^{14} O^7$, is prepared in the same manner as æthylotannaspidic acid. It forms a bright purple-violet powder, or a dark, resinous, tenacious mass, according to the amount of water used in the precipitation. It has a faint odour, which is peculiar, but not agreeable, and dissolves readily in æther and strong alcohol with a very deep purple colour. On evaporating the solution, a resinous, shining, blackish-purple substance is left; the solution is decomposed with time, and anhydrous pteritannic acid is then contained in the liquid; an addition of a small quantity of hydrochloric acid prevents or delays this decomposition. It has scarcely any reaction upon blue litmus-paper; a solution of gelatine is scarcely rendered turbid; the alcoholic solution furnishes, with neutral and basic acetate of lead, beautiful green precipitates, which, after washing and drying, yield violet-gray powders. Chlorides of barium and calcium cause no turbidity, but on the addition of a few drops of ammonia a green precipitate. Protochloride of iron with ammonia and the acetate of the peroxide of iron give blackish-green, acetate of copper a violet, chloride of aluminium a very beautiful blue-violet precipitate on the addition of a little ammonia; otherwise it merely colours the liquid lilac. Protochloride of tin turns the liquid violet; ammonia then produces a bluish-green precipitate in it. In dilute potash and ammonia the acid dissolves with a beautiful green colour, but very soon decomposition ensues, and it turns brown. Sulphuric acid dissolves it with a brown colour; water precipitates it unaltered from the solution. Chlorine and nitric acid destroy it; sulphuretted hydrogen has no action upon it. The compound precipitated in the form of a red powder furnished on analysis—

Carbon	65·66	65·90	65·65	52 =	3900	65·82
Hydrogen ..	7·12	7·21	7·35	34	437·5	7·17
Oxygen....	27·22	26·89	27·00	16	1700	27·01

The resinous æthyle compound gave, on the other hand—

Carbon	67·03	52 =	3900	67·09
Hydrogen	7·05	33	412·5	7·09
Oxygen	25·92	15	1500	25·82

leading to the formula $C^4 H^5 O, 2C^{24} H^{14} O^7$.

Æthylopteritannate of Lead.—On precipitating the acid with an alcoholic solution of acetate of lead, avoiding an excess of the latter, a green precipitate falls, which contains 10·50 per cent. of oxide of lead, the formula $C^{104} H^{67} O^{31}, PbO$ requires 10·62. When the solution is mixed with an insufficient quantity of basic acetate of lead, and the precipitate digested at the ordinary temperature with an excess of neutral acetate of lead, a compound is obtained with 21·55 per cent. oxide of lead; the formula $C^4 H^5 O, PbO, 2C^{24} H^{14} O^7$ requires 19·05. With an excess of basic acetate of lead the precipitate soon becomes greenish-brown. It furnished 33·25 and 33·93 per cent. oxide of lead.

Alcohol extracts from the root of the fern a species of sugar. When the extract is precipitated with hydrochloric acid, and after filtration with acetate of lead, the brown precipitate separated, and the excess of lead removed from the solution with sulphuretted hydrogen, the filtered liquid leaves on evaporation a brown syrup, which has at first a sweet, but subsequently nauseous taste. This sugar reduces oxide of copper from the solution in potash.

The author leaves it undecided to which of these constituents the medicinal effects of the fern-root should be ascribed. He recommends the use of æther free from alcohol for the preparation of the officinal *extractum filicis*, which dissolves out only the filicic acid, pteritannic acid and fatty oil. If the æther contains alcohol, it also extracts some tannaspidic acid and sugar, which soon begin to decompose.—*Jahrb. für Prakt. Pharm.*, xii. p. 129.

On the Salts of Permanganic Acid.
By MM. Personne *and* Lhermite.

The authors have investigated a series of permanganates, and have arrived at results which completely confirm those of Mitscherlich. Mitscherlich decomposed the permanganate of potash by nitric acid; the permanganic acid was then decomposed by heat into oxygen and peroxide. The authors found that the formed nitre always contained a small quantity of protonitrate of manganese, and therefore suspected that the composition of the permanganates had not been quite correctly ascertained; they consequently decomposed the permanganates with a muriatic solution of arsenious acid, and then determined the base and the manganese in the salts of the protoxide of manganese produced. This method is more accurate, but it furnished the same results as Mitscherlich obtained.

The authors propose the employment of permanganate of potash for determining the amount of free alkali in a liquid, provided this does not contain too large an amount of reducing agents. When the salt is not further reduced than to the state of green

manganate of potash, and a solution of bicarbonate of potash is added to the solution from a graduated tube until the liquid again acquires a red colour, the half of the carbonic acid corresponds to the amount of free alkali.—*Journ. de Pharm. et de Chim.*, xxix. pp. 115, 161.

On the Application of Benzine to the Separation of Fatty Matter in Dyeing. By M. Collas.

The carbo-hydrogen known under this name, which may be obtained at a small cost from the products of the gas factories, serves advantageously to dissolve the fats, resins, &c. out of textile materials. Nitrobenzine, as is known, has been used for some time in the manufacture of perfumery. Its odour is that of oil of bitter almonds.—*Bulletin. de la Soc. d'Encouragement*, xv. July 1851, p. 387.

On Gutta Percha. By M. Arppe.

According to the author, gutta percha differs in composition from caoutchouc. He considers it to be a mixture of resins, which may have been formed from a carbo-hydrogen, $C^{10} H^8$.

Gutta percha, when separated from mechanical admixtures, is soluble in æther which is free from alcohol. If it has been previously treated with alcohol, it does not dissolve in æther any longer.

It contains small quantities of volatile matters; the distillate with water is brown, and has a peculiar unpleasant smell. It consists essentially of six different resins:—

α-Resin is obtained by extracting gutta percha with alcohol of 0·81 spec. grav. 13 per cent. of the gutta percha is dissolved. The solution is evaporated, and treated with cold æther; the α-resin remains in the form of a white powder. It is difficultly soluble in alcohol of 0·81 spec. grav., and separates from such a solution on evaporation in confused crystalline plates, which require a high temperature to melt, but then decomposing, and giving products which burn with a brilliant smoky flame.

β-Resin, $C^{40} H^{31} O^6$.—The æther, which in the previous process left α-resin undissolved, took up β-, γ-, δ-resins. On evaporating the solution, a glutinous mass remains, which dissolves completely in boiling anhydrous alcohol, with the exception of a white powder, which appears to be a combination of the δ-resin with lime. The alcoholic solution contains two resins, which after the evaporation of the alcohol appear as a glutinous mass mixed with crystals. The more soluble uncrystalline resin may be separated from the crystalline β-resin by cold anhydrous alcohol. The latter then crystallizes in needle-like prisms, half a line in length, which lose their lustre on the addition of alcohol, fall to powder, and then dissolve. Resin β melts at 257° F., and solidifies to a colourless glassy mass; its alcoholic solution has no acid reaction, and is not precipitated by acetate of lead; its ætherial solution does not expel the carbonic acid from carbonate of potash.

γ-Resin, $C^{40} H^{31} O^3$.—This is separated from the above resin by cold alcohol, in which γ-resin is easily soluble. It is glutinous, re-

tains the alcohol obstinately, melts at 122° F., and is then light yellowish-brown, becoming darker on exposure to the air. It gradually loses its tenacity in water, and is converted into white flocks, which are difficultly soluble in alcohol. It gives with acetate of lead a light brown butyraceous precipitate, which melts at 212° F.

δ-Resin, $C^{40}H^{24}O^{8}$.—This is obtained by boiling the substance left by alcohol of 0·81 spec. grav. with alcohol of 0·83 spec. grav., evaporating the solution, and treating the residue with cold water; it is soluble in æther, and forms on evaporation a glutinous mass. It is deposited in colourless granules by exposing an alcoholic solution to cold. It melts at 347° F. δ-resin is readily soluble in æther, difficultly soluble in cold anhydrous alcohol, and is not precipitated by acetate of lead.

ε-Resin, $C^{40}H^{31}O^{10}$.—This, together with the following ζ-resin, constitutes the part insoluble in alcohol; they amount together to 87 per cent. of the whole substance. In order to obtain these two resins, the gutta percha is dissolved in æther, evaporated, and thoroughly extracted by alcohol. As the ε-resin is more readily soluble in æther than the ζ-resin, it may be obtained from the first quantities of æther with which the mixtures are treated. It is a snow-white powder, melts at 131° F., forming on cooling a transparent, yellow, brittle mass, is precipitated from the solution in æther by addition of alcohol, and dissolves to a very slight extent in boiling alcohol.

ζ-Resin, $C^{40}H^{31}O^{7}$, is contained in the later portions of æther with which the mixture of ε and ζ is treated. It is a white, rather soft, although brittle mass, which is difficult to powder. It melts at 104° F., and is then yellowish-brown, glutinous, and may be drawn out in threads. At 212°–230° it is brown, and on cooling brick-red, destitute of lustre, and resembles raw gutta percha, of which it is the chief constituent. It is almost insoluble in cold æther, and very slightly soluble in boiling alcohol.

The products of the dry distillation of gutta percha are different from those of caoutchouc.—*Journ. für Prakt. Chem.*, vol. liii. pp. 171–174.

On the Treatment of the Fatty Substances used for making Candles. *By* MM. Masse *and* Tribouillet.

The fats are known to form a kind of soap with sulphuric acid. These manufacturers heat the fats with sulphuric acid, or mix them together mechanically, wash the mass, and introduce it into a distillatory apparatus, where it is heated up to 392°–482° F., and high-pressure steam passed through, by means of which the fatty acids are distilled over. When palm-oil is used, the effect of this treatment is the following:—The fat itself melts at 86° F., after treatment with sulphuric acid at 100°·4 F., after washing with water at 112° F., and after distillation at 114°·8 F. The product which passes over first melts at 130° F., but afterwards the melting-point sinks, and the products become more and more crystalline. After pressing the whole distillate, the melting-point of the cake is 130° F., the

same as the part passing over at the commencement of the operation. In the original paper the details of treatment of other fats are given. The process is recommended by the Commission of Examination.—*Bullet. de la Soc. d'Encour.*, xv. July 1851, pp. 392–399.

ANALYTICAL CHEMISTRY.

Quantitative Determination of Phosphoric Acid. By M. Ullgren.

The author has adopted the two following methods of separating phosphoric acid in the analysis of metallic iron and iron ores, and obtained satisfactory results.

According to the first method, the nitric acid solution is evaporated to the thickness of a syrup after the addition of a little hydrochloric acid. This solution, somewhat diluted, is poured, with constant stirring, into a solution of sulphuret of potassium and silicate of potash, the former of which must be present in larger quantity than is sufficient to precipitate the iron; for every gramme of iron 5 grms. of sulphuret of potassium (prepared by igniting 1 part of soot with $3\frac{1}{2}$ parts of sulphate of potash) and 1 grm. of silica glass (prepared by melting 1 part of powdered quartz with $2\frac{1}{2}$ parts of a mixture of 5 parts of carbonate of potash and 4 parts of carbonate of soda). The precipitate contains the whole of the electro-positive metals in the form of sulphurets, and the lime, magnesia, and alumina as silicates; while the solution contains phosphate of potash and the sulphur salts of the electro-negative metals. Upon filtering, a clear liquid passes at the commencement, afterwards becoming greenish and cloudy; this may however be prevented by a previous addition of fresh-precipitated hydrated oxide of lead in sufficient quantity. By this means the electro-negative sulphurets are removed by the decomposition of the sulphuret of potassium by the oxide of lead. The precipitate upon the filter is then washed with water containing one-tenth of its volume of a tolerably-concentrated solution of carbonate of ammonia and some caustic ammonia. The liquid is evaporated almost to dryness, the residual mass moistened with hydrochloric acid, diluted with water, heated for an hour, and then filtered to separate the silicic acid. The filtrate contains the phosphoric acid, and almost always minute traces of a metal which in certain characters resembles iron, and has already been described by the author under the name of aridium*. It is mixed with tartaric acid, by which the precipitation of that oxide is prevented, and the phosphoric acid separated in the usual manner, by sulphate of magnesia.

The second method is based upon the property of the ammoniophosphate of magnesia to remain dissolved in small quantities in ammoniacal solutions of tartrate of iron, but not in ferridcyanide of potassium. In the first place, two concentrated solutions are prepared, the one of 8 grms. of tartaric acid, the other of 14 grms. of cyanide of potassium. 1 grm. of the iron is then dissolved in nitric

* Chem. Gaz., vol. viii. p. 289.

acid, with the addition of a little hydrochloric acid. The tartaric acid solution is then added to that of the iron; a sufficient quantity of sulphate of magnesia is next added, then a large excess of ammonia, and finally the solution of cyanide of potassium. To this deep red liquid a concentrated solution of sulphuret of potassium is carefully added, until the colour, which at first changes to bright yellow, again becomes dark. After the lapse of a few hours, a precipitate forms in the glass, which contains the whole of the phosphoric acid combined with ammonia and magnesia mixed with a little sulphur. It is washed with ammoniacal water, dried, heated until the sulphur ignites, and then melted with carbonate of potash and soda in a platinum crucible. The melted mass is boiled with water, the solution filtered, then made strongly acid with hydrochloric acid, and evaporated, in which operation the pyrophosphoric acid is converted into ordinary phosphoric acid. After the addition of tartaric acid and excess of ammonia, the phosphoric acid is precipitated by magnesia salts. The liquid must be of a dark colour for the experiment to be successful; it then retains in solution all the electro-negative metals which may be mixed with the iron.

If, however, lime is present in an iron ore, the above methods must be altered. The first part of the process is the same; but instead of using a solution of a magnesia salt, chloride of calcium is to be used, in order that the whole of the phosphoric acid may combine with lime. The phosphate of lime is then decomposed by sulphuric acid, the sulphate of lime separated by means of alcohol, the filtrate saturated with ammonia, tartaric acid added, and finally a solution of a magnesian salt. The cyanide of potassium which is employed in this process must be carefully examined for phosphoric acid before being used, and in case it is present must be separated by the addition of ammonia and a lime or magnesia salt.—*Journ. fur Prakt. Chem.*, vol. liii. pp. 33–37.

On a new Method of determining Carbonic Acid, and on the Amount of this Acid in the Atmosphere. By M. Mène.

The following is the method proposed by the author:—In examinations of the atmosphere, a large aspirator draws the air through a corked bottle containing an accurately-measured quantity of solution of caustic potash. A glass tube, drawn out at the lower end, and through which the air is conducted into the potash, is fitted into the cork of the bottle. When the aspirator has emptied itself, the fine end of the tube is rinsed with a little distilled water, a few drops of solution of litmus added to the potash, and now so much of a standard solution of acid added from a graduated burette as to turn the liquid wine-red. The number of degrees of the burette is now noted, and the analysis finished when the colour is brownish-red; the number of degrees is now noted again and the amount of carbonic acid which the potash contains calculated. As the potash itself contains some carbonic acid, this is first determined, and for this reason a fixed quantity of solution of potash is poured into the bottle.

By means of this method the author found, in an investigation made in the month of August 1851 :—

		Temperature of the air.	Carbonic acid.	Carbonic acid. in 1 litre of air.
4th Aug.	8–9 morning....	68° F.	0·036	0·00034
	12–1 afternoon ..	75°	0·041	0·00042
	5–6 evening....	70°	0·026	0·00027
5th Aug.	8–9 morning....	71°	0·012	0·00012
	12–1 afternoon ..	75°	0·023	0·00027
	4–5 evening	71°	0·035	0·00029
6th Aug.	7–8 morning....	62°	0·013	0·000132
	12–1 afternoon ..	80°	0·032	0·00036
	7–8 evening	73°	0·030	0·000299
7th Aug.	8–9 morning....	68°	0·014	0·000125
	1–2 afternoon ..	78°	0·033	0·00034
	5–6 evening	70°	0·009	0·000112

The author states, that, in comparing his method with the ordinary one, in which the air is first passed through tubes to be dried, and then through the ordinary potash-apparatus, he has found that the latter gives the amount of carbonic acid somewhat too high, it being exceedingly difficult to dry the air so completely that it shall not yield some aqueous vapour to the potash.—*Comptes Rendus*, xxxiii. p. 223.

PROCEEDINGS OF SOCIETIES.

Chemical Society of London.

The meetings were commenced for the season on Monday, Nov. 3, in the new rooms of the Society, at 5 Cavendish Square, when papers were read on the following subjects :—

"Observations on the Phænomena of Animal Phosphorescence." By Thornton J. Herapath.

Reference is made in this paper to the opinion, which appears to have prevailed among scientific men, that the phosphorescence of animals is due to a slow combustion of phosphorus contained in the animal structures. With the view of testing the accuracy of this opinion, experiments were made with glow-worms, which were confined in glass vessels while emitting the phosphorescent light, and means adopted to ascertain whether any ozone was produced under these circumstances. The results being uniformly negative, it was concluded that the phosphorescence of the glow-worm is not caused by the presence of phosphorus in the luminous matter, and that a similar inference may be drawn with reference to the phænomena of vital phosphorescence generally. The author hazards an opinion, unsupported however by direct evidence, that the phænomena in question are due to the existence in the luminous matter of carbon in a different allotropic condition from any now recognised. This view, he states, accords in some respects, although not entirely, with

that entertained by Matteucci, who attributes animal phosphorescence to the slow combustion in air of a substance, *sui generis*, principally composed of carbon, hydrogen, oxygen and nitrogen.

"Analysis of a Mineral containing Gold, from the Province of Coquimbo, Chili." By F. Field.

The mineral described is similar to various classes of gray antimonious copper, found in many parts of Chile. It was found on analysis to contain in 100 parts—

Gold	0·003
Silver	0·075
Copper	36·720
Iron	1·232
Zinc	7·260
Antimony	20·284
Arsenic	3·912
Sulphur	30·350
	99·836

"Description of Lapis Lazuli, found in large quantities in the Cordilleras of the Andes." By F. Field.

Immense masses of a bright blue rock having been found by a miner, it was at first supposed to consist of carbonate of copper. Analysis however proved that it contained no copper, but was a true lapis lazuli. It was interspersed with small veins of pure carbonate of lime. Analysis gave in 100 parts—

Silica	37·60
Alumina	11·21
Sulphur	1·65
Iron	0·08
Magnesia	0·36
Soda	9·66
Carbonic acid	15·05
Lime	24·10
	99·71

"On the spontaneous Decomposition of Gun-Cotton, and its Congeners." By J. H. Gladstone, Ph.D.

The author, having had occasion, some time ago, to prepare a variety of samples of the different substances produced by the action of nitric acid on woody fibre, starch, sugar, gum, &c., and having found that several of the samples, after being kept for some time, had undergone either partial or complete decomposition, describes the phænomena which were observed in each instance. From the observations recorded the following general conclusion is drawn with reference to the spontaneous decomposition of gun-cotton and its congeners,—that substances of this character have a tendency to suffer alteration in process of time from half the oxygen of the NO^4, they contain, separating from the remaining NO^2, which escapes as nitric oxide gas, and combining with the organic substance, so as to form non-azotized acids, oxidizing at the same time a portion of the hydrogen, and causing it to be given off as water.

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